(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号

特開平11－169726

(43)公開日　平成11年(1999)６月29日

(51)Int.Cl.⁶	識別記号	ＦＩ	
ＢＯ１Ｊ　35/02		ＢＯ１Ｊ　35/02	Ｊ
21/04		21/04	Ｍ
21/06		21/06	Ｍ
23/02		23/02	Ｍ
23/06		23/06	Ｍ

審査請求　未請求　請求項の数18　ＯＬ　（全８頁）　最終頁に続く

(21)出願番号　特願平10－240010

(22)出願日　平成10年(1998)８月26日

(31)優先権主張番号　特願平9－231951

(32)優先日　平９(1997)８月28日

(33)優先権主張国　日本（ＪＰ）

(71)出願人　000010087
東陶機器株式会社
福岡県北九州市小倉北区中島２丁目１番１号

(72)発明者　久我　辰彦
福岡県北九州市小倉北区中島２丁目１番１号　東陶機器株式会社内

(72)発明者　小林　秀紀
福岡県北九州市小倉北区中島２丁目１番１号　東陶機器株式会社内

(72)発明者　佐伯　義光
福岡県北九州市小倉北区中島２丁目１番１号　東陶機器株式会社内

(74)代理人　弁理士　小山　有　（外１名）

(54)【発明の名称】　光触媒作用を有する機能材及び複合機能材とそれらの製造方法

(57)【要約】

【課題】　光触媒活性点またはその近傍に貴金属等を担持せしめて光触媒活性の向上を図る。

【解決手段】　光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合し、この混合が終了した後に、若しくは混合と同時に、混合溶液に紫外線を照射することで、光触媒粒子の光活性点上に電子を生じさせ、この電子によって光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめる。

【特許請求の範囲】

【請求項１】 光触媒の表面に光触媒活性を助長する金属または金属化合物が担持された光触媒作用を有する機能材であって、前記金属または金属化合物は光触媒活性点またはその近傍に担持されていることを特徴とする光触媒作用を有する機能材。

【請求項２】 請求項１に記載の光触媒作用を有する機能材において、前記光触媒の表面に担持される光触媒活性を助長する金属または金属化合物が光触媒表面を被覆する表面被覆率は５％以下であることを特徴とする光触媒作用を有する機能材。

【請求項３】 請求項１または請求項２に記載の光触媒作用を有する機能材において、前記光触媒は、TiO_2、$SrTiO_3$、ZnO、SiC、GaP、CdS、CdSe、MoS_3のうちの少なくとも１種であり、前記光触媒活性を助長する金属または金属化合物は、Cu、Ag、Ni、Zn、Co、Fe、Pt、Pdまたはこれらの化合物のうちの少なくとも１種であることを特徴とする光触媒作用を有する機能材。

【請求項４】 請求項１乃至請求項３のいずれかに記載の光触媒作用を有する機能材であって、更に水酸基を化学吸着する性質を持つ化合物を添加することにより、水酸基を光触媒及び添加物表面に化学吸着させて、その保持した水酸基にて親水性を長期にわたり発揮することを特徴とする光触媒作用を有する機能材。

【請求項５】 請求項４に記載の光触媒作用を有する機能材であって、前記添加成分が前記光触媒が有する湿潤熱と同等以上の湿潤熱を有する化合物であることを特徴とする光触媒作用を有する機能材。

【請求項６】 請求項４に記載の光触媒作用を有する機能材であって、前記添加成分が、SiO_2、Al_2O_3、GeO_2、ThO_2、ZnOから選ばれた少なくとも１つの金属化合物であることを特徴とする光触媒作用を有する機能材。

【請求項７】 光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合し、この混合が終了した後に、混合溶液に紫外線を照射することで、光触媒粒子の光活性点上に電子を生じさせ、この電子によって光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめるようにしたことを特徴とする光触媒作用を有する機能材の製造方法。

【請求項８】 光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合しつつ紫外線を照射することで、光触媒粒子の光活性点上に電子を生じさせ、この電子によって光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめるようにしたことを特徴とする光触媒作用を有する機能材の製造方法。

【請求項９】 請求項７または請求項８に記載の光触媒作用を有する機能材の製造方法において、前記混合溶液に対する紫外線の照射エネルギ（照射時間×光源強度）を、０．３Ｊ／cm^2以上６０Ｊ／cm^2以下とすることを特徴とする光触媒作用を有する機能材の製造方法。

【請求項１０】 請求項１乃至請求項６に記載の機能材を、基材表面に設けたことを特徴とする光触媒作用を有する複合機能材。

【請求項１１】 請求項１０に記載の光触媒作用を有する複合機能材において、前記機能材がバインダを介して基材表面に設けられていることを特徴とする光触媒作用を有する複合機能材。

【請求項１２】 請求項１１に記載の光触媒作用を有する複合機能材において、前記機能材がバインダ中に混合分散されていることを特徴とする光触媒作用を有する複合機能材。

【請求項１３】 請求項１１に記載の光触媒作用を有する複合機能材において、前記バインダは無機化合物または有機化合物であることを特徴とする光触媒作用を有する複合機能材。

【請求項１４】 請求項１０乃至請求項１３に記載の光触媒作用を有する複合機能材において、前記基材が陶磁器製品であることを特徴とする光触媒作用を有する複合機能材。

【請求項１５】 請求項１０乃至請求項１３に記載の光触媒作用を有する複合機能材において、前記基材がガラスであることを特徴とする光触媒作用を有する複合機能材。

【請求項１６】 請求項７乃至または請求項８に記載した機能材の製造方法によって機能材を製造し、この機能材を基材の表面に塗布した後、５００℃以上９００℃以下で加熱することを特徴とする光触媒作用を有する複合機能材の製造方法。

【請求項１７】 請求項７乃至または請求項８に記載した機能材の製造方法によって機能材を製造し、また、基材の表面にバインダを塗布し、このバインダの上に前記機能材を塗布した後、５００℃以上９００℃以下で加熱することを特徴とする光触媒作用を有する複合機能材の製造方法。

【請求項１８】 請求項７乃至または請求項８に記載した機能材の製造方法によって機能材を製造し、この機能材をバインダ中に分散した後、基材の表面に塗布し、更にその後、７０℃以上１５０℃以下で加熱することを特徴とする光触媒作用を有する複合機能材の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は光触媒作用を有する機能材とその製造方法、またこの機能材を表面に形成した複合機能材とその製造方法に関する。

【０００２】

【従来の技術】TiO_2などの光触媒に紫外線を照射すると、電子と正孔を生じ、これらが関与する反応が起こる

ことが従来から知られている。更に、最近では光触媒粒子に遷移金属や貴金属の微粒子を担持させることで光触媒活性が向上することが分かっている。

【0003】そして、貴金属の微粒子等を光触媒粒子に担持させる方法として、以下の公報に開示される方法が知られている。即ち、特開平8－243390号公報には、水熱合成法で調製したチタニアに、貴金属を焼成によって担持させる方法が開示されている。また、特開平8－283022号公報には、Pt等の金属を含むTi原料を加熱溶融せしめ、蒸発した原料を酸素と反応させることで、アナターゼ型TiO_2及びルチル型TiO_2の微粒子表面にPt等の金属超微粒子が突出した複合微粒子を製造することが開示されている。また、特開平8－283023号公報にはPt等の金属を含むTi原料を水素ガスを含む不活性ガス雰囲気で加熱溶融せしめ、TiとPt等の金属からなる超微粒子を生成し、更にこの超微粒子を大気中で熱処理することでPt等の金属またはその酸化物が均一に分散した複合微粒子を製造することが開示されている。また、特開平9－132432号公報には有機溶剤中にチタン化合物と銅化合物を溶解させ、この溶液を焼成することでアモルファス構造のコーティング膜を形成する方法が開示されている。

【0004】

【発明が解決しようとする課題】光触媒の作用は、紫外線などが照射されることで、価電子帯にあった電子（e^-）が伝導帯に励起され、価電子帯には正孔（h^+）が生じ、これら電子（e^-）及び正孔（h^+）が酸化還元反応等を促進すると考えられる。そして、貴金属の微粒子を担持することで、発生した電子と正孔の分離が促進され、光触媒活性が向上する。

【0005】一方、光触媒粒子には活性点が存在し、この活性点に貴金属等の微粒子が担持されることで、光触媒活性の向上が図れ、活性点以外の箇所に微粒子が担持されると却って光触媒活性を阻害する。しかしながら、従来方法にあっては、いずれも活性点のみを選定して貴金属等の微粒子を担持させることができない。

【0006】

【課題を解決するための手段】上記課題を解決すべく本発明に係る光触媒作用を有する機能材は、請求項1にあっては、光触媒の表面に光触媒活性を助長する金属または金属化合物が担持された光触媒作用を有する機能材であって、前記金属または金属化合物は光触媒活性点またはその近傍に担持された構成とした。このような構成とすることで、光触媒活性の向上を図ることができる。尚、光触媒の形状としては、粒子状に限らず、板状、多孔体等任意である。

【0007】また、光触媒活性を助長する金属または金属化合物の全表面に対する占有面積が大きすぎると、光触媒活性点の光吸収効率が低下し光触媒活性が低下する。したがって、表面被覆率は5％以下、好ましくは0．25％以上1％以下とすることが好ましい。

【0008】また、前記光触媒としては例えば、TiO_2、$SrTiO_3$、ZnO、SiC、GaP、CdS、CdSe、MoS3のうちの少なくとも1種が挙げられ、前記金属または金属化合物としては例えば、Cu、Ag、Ni、Zn、Co、Fe、Pt、Pdまたはこれらの化合物のうちの少なくとも1種が挙げられる。

【0009】更に、光触媒作用を有する機能材としては、水酸基を化学吸着する性質を持つ化合物を添加してもよい。このようにすることで、親水性を長期にわたり発揮することが可能になる。このための添加成分としては、光触媒が有する湿潤熱と同等以上の湿潤熱を有する化合物、例えば、SiO_2、Al_2O_3、GeO_2、ThO_2、ZnO等が好ましい。

【0010】また、本発明に係る光触媒作用を有する機能材の製造方法は、光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合し、この混合が終了した後に、混合溶液に紫外線を照射することで、光触媒粒子の光活性点上に電子を生じさせ、この電子によって光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめる。金属塩としては、塩化物、硝酸塩、硫酸塩等の形態が考えられる。

【0011】また、本発明に係る光触媒作用を有する機能材の別の製造方法は、光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合しつつ紫外線を照射することで、光触媒粒子の光活性点上に電子を生じさせ、この電子によって光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめる。

【0012】このように、光還元法を利用することで、光活性点若しくはその近傍のみに、貴金属等の微粒子を析出せしめることができる。

【0013】また、混合溶液に対する紫外線の照射エネルギ（照射時間×光源強度）としてはを、0．3J／cm^2以上60J／cm^2以下とするのが好ましい。この範囲を外れると、活性が低下する。

【0014】また、本発明に係る光触媒作用を有する複合機能材は、前記した機能材を、基材表面に設けた。機能材を基材表面に固定する手段としては、例えば無機化合物または有機化合物からなるバインダを用いる。バインダの使用態様としては、バインダを機能材と基材表面の間に介在せしめる他にバインダ中に機能材を混合分散してもよい。また基材としては、例えば、陶磁器製品やガラスが挙げられる。

【0015】更に、本発明に係る光触媒作用を有する複合機能材の製造方法は、先ず、前記した方法で機能材を製造し、この機能材を基材の表面に塗布した後、500℃以上900℃以下で加熱する。また、機能材を基材の表面に塗布する前に、基材表面にバインダを塗布してお

き、このバインダの表面に機能材を塗布するようにしてもよい。更に、バインダ中に機能材を混合分散し、このバインダを基材表面に塗布する場合には、バインダを基材表面に塗布した後、７０～１５０℃で加熱する。

【００１６】

【発明の実施の形態】（実施例１）石原産業製の酸化チタンゾル（ＳＴＳ－１１：TiO_2濃度１５％）に、塩化亜鉛、塩化鉄（＝）、塩化ニッケル、塩化銅、酢酸銅の０．５ｗｔ％水溶液を適量添加した。このとき、添加した金属の量は、添加した金属全てが析出したと仮定して、担持金属の酸化チタン粒子被覆率が約０．５％になるようにした。この後、上記の水溶液を水道水で希釈し、TiO_2濃度が０．７５％になるように調整し、紫外線を４０Ｊ／ｃm_2だけ照射し、金属をTiO_2表面に担持させた。そして、金属をTiO_2表面に担持した溶液を、釉薬が付与された焼成済タイル表面または無釉の焼成済タイル表面に長石や炭酸カリウム等からなるフリットをコーティングしたものの上に２．２×10^{-3}ｇ／ｃm^3だけ塗布し、８８０℃で焼き付けた。得られた試料の光触媒活性を、硝酸銀の呈色量と油分解性能により評価した。また、比較例として、金属を添加しないTiO_2単層の焼き付け膜と、金属を単に混合しただけ（光還元法による析出なし）の酸化チタンゾルの焼き付け膜を作製し、同様の評価をした。結果を以下の（表１）に示す。

【００１７】

【表１】

	金属光還元担持系				金属単純混合系	単層
	Fe/TiO2	Sn/TiO2	Ni/TiO2	Cu/TiO2	TiO2+Cu	TiO2
硝酸銀呈色による光触媒活性指標	5	4	3.8	4.2	1.5	1
抗菌力指標	1.8	1.8	1.7	1.8	1.4	1
油分解性(%)	65	55	70	70	35	30

評価方法

１．$AgNO_3$による
光触媒活性指標：１％の$AgNO_3$ａｑを試験体に塗布し、紫外線ランプ（１．５ｍW／ｃm^2）を３００sec照射し、光還元による銀呈色度によって光活性を評価した。

２．抗菌力指標　：酸化チタン単層の試験体の抗菌力を１として抗菌力を比較した。

３．油分解率　：試験体に１ｍｇ／１００ｃm^2だけサラダ油を塗布し、１ｍW／ｃm^2の紫外線を７日間照射した。油塗布前、油塗布直後、油塗布光照射後の光沢を測定し、下式により油分解率を求めた。

$$\text{油分解率}=\frac{|(\text{光照射後光沢})-(\text{油塗布直後光沢})|}{|(\text{油塗布前光沢})-(\text{油塗布直後光沢})|}\times 100$$

【００１８】（表１）より、本発明方法によって得られた膜は、何れの金属を添加した場合であっても、TiO_2単層はもとより、Cu単純混合系の被膜より光触媒活性が高いことが分る。

【００１９】（実施例２）光触媒活性に及ぼす担持金属量の効果を以下の実験で調べた。先ず、（実施例１）と同様な方法で、酸化チタン粒子表面に酢酸銅を出発塩としてCuを担持せしめた。ただし、Cuの担持量は光触媒表面の被覆率で０～２０％の範囲で変化させた。得られた試料の光触媒活性を、硝酸銀の呈色値と油分解性能により評価した。また、比較例として、添加金属量を一定とした単純混合型酸化チタン焼き付け膜を作製し、同様の評価を行った。結果を図１及び図２に示す。

【００２０】図１及び図２から、被覆率が１０％となるような過剰にCuを添加した場合には、硝酸銀の呈色値と油分解性能が大幅に低下し、特に被覆率が０．２５～１％の範囲で硝酸銀の呈色値と油分解性能が良好で、この範囲を超えると、急激に硝酸銀の呈色値と油分解性能が劣化することが分る。

【００２１】（実施例３）光触媒活性に及ぼす金属担持工程の紫外線の照射エネルギ量（照射時間×光源強度）の影響について実験した。先ず、（実施例１）と同様な方法で、酸化チタン粒子表面に酢酸銅を出発塩としてＣｕを担持せしめた。ただし、金属担持のエネルギ量を０～１２０Ｊ／ｃm^2で変化させた。結果を図３に示す。

【００２２】図３から、照射エネルギが８０Ｊ／ｃm^2となると却って光触媒活性が低下することが分る。そして、紫外線の照射エネルギ量としては、０．３Ｊ／ｃｍ

^{2}～６０Ｊ／ｃｍ^{2}が適当であることも分る。

【００２３】（実施例４）金属を担持した光触媒粒子で基材表面に光触媒活性を付与する実験を行った。先ず、石原産業製の酸化チタンゾル（ＳＴＳ－１１：TiO_2濃度１５％）に、酢酸銅水溶液（０．５ｗｔ％）を添加した。尚、添加した金属の量は、添加した金属全てが析出したと仮定して、担持金属の酸化チタン粒子被覆率が約０．５％になるように調整した。この後、水道水で更に希釈してTiO2濃度が０．７５％になるようにし、攪拌しながら紫外線を４０Ｊ／ｃｍ^{2}だけ照射し、TiO_2粒子表面にCuを担持させた。これを７ｍｍのガラスビーズにディッピング法で塗布し、６５０℃で焼き付けて光触媒ビーズを作製した。上記の光触媒ビーズ（直径７ｍｍ）８０ｇを、図４に示すように容器内に入れ、赤色染料（エオシンＹ：２ｐｐｍ、２００ｍｌ）の分解を行った。比較例として、金属を担持しないTiO_2単層コーティングと金属の単純混合型のコーティングを施したガラスビーズについても同様の試験を行った。結果を以下の（表２）に示す。尚、（表２）における分解率は染料の色落ち具合を示す。

【００２４】

【表２】

	Cu光還元担持 TiO2コーティング	Cu単純混合 TiO2コーティング	TiO2単層
分解率(%)	45	25	20

【００２５】（表２）から、光還元法にてCuを析出して担持せしめたTiO_2コーティングは赤色染料の分解において高い活性を示す。

【００２６】（実施例５）先ず、（実施例１）と同様な方法で、酸化チタン粒子表面に酢酸銅を出発塩としてＣuを担持せしめ、これにシリコーン樹脂（信越化学ＫＰ８５８）を混合した。そして、酸化チタンとシリコー樹脂の固形分比を７：３とした後、エタノールにて総重量を３倍希釈してコーティング液とした。一方、基材はタイルを用い、スピンコーティング法（基板にコーティング液を滴下した後基板を回転させ、遠心力にて拡散させて均一な被膜を形成する方法）によりコーティング液を塗布した後、１５０℃で３０分程バインダを熱硬化させた。　得られた試料体の光触媒活性を抗菌性に評価した。比較例については、Cu単純混合型の酸化チタンゾル及び酸化チタン単味ゾルを用い、上記したシリコーン樹脂バインダを用いて作製した。結果を以下の（表３）に示す。

【００２７】

【表３】

	本発明	単純混合	ＴｉＯ₂単層
抗菌力指標	３	１．５	１

＊抗菌力指標は酸化チタン単層の試験体の抗菌力を１として比較した。

【００２８】（表３）からシリコーン樹脂に本発明に係る機能材を混合した場合でも、光触媒活性が向上することが分る。

【００２９】（実施例６）実施例５と同様な方法で、Ｃuを担持した酸化チタン粒子とバインダとしてのシリコーン樹脂を含むコーティング液を調製した。一方基材は、予めシリコーン樹脂でコーティングしたアクリル板を用い、スピンコーティングにより、コーティング液を塗布した後、８０℃で３０分程バインダを熱硬化させた。得られた試験体の光触媒活性を抗菌性により評価した。比較例については、Cu単純混合型の酸化チタンゾル及び酸化チタン単味ゾルを用い、上記したシリコーン樹脂バインダを用いて作製した。結果を以下の（表４）に示す。

【００３０】

【表４】

	本発明	単純混合	ＴｉＯ₂単層
抗菌力指標	２．３	１．４	１

【００３１】（表４）からも、（実施例５）と同様に、シリコーン樹脂に本発明に係る機能材を混合した場合でも、光触媒活性が向上することが分る。

【００３２】（実施例７）変色率について実験を行っ

た。ここで、変色率＝変色色差／飽和変色色差である。先ず、酸化チタン濃度が０．７５％のゾルに酢酸銅を添加しながら紫外線を照射した。添加する銅量、紫外線照射が増えると、変色色差は増大したが、酢酸銅／酸化チタン＝１５％、紫外線照射時間４８時間で変色は頭打ち（飽和）となった。この時の変色色差を飽和変色色差とする。次に、酸化チタン濃度が０．７５％のゾルに銅の酸化チタン被覆率が０．５％になるように酢酸銅を添加して紫外線（０．８mW／cm^2）を照射し、経時的に変色色差を求めた。そして、変色率を算出した結果を図５に示す。また、酸化チタン濃度が０．７５％のゾルに、金属被覆率が０．１～７．５％になるように酢酸銅を添加し、紫外線（０．８mW／cm^2）を１８時間照射し、変色率と金属被覆率との関係を試験した。結果を以下の（表５）に示す。

【００３３】

【表５】

金属被覆率(%)	0.001	0.01	0.1	0.5	5	7.5
変色率(ΔE)	8	16	22.3	56.4	84	100

【００３４】先ず、図５から照射時間が２０時間を超えると、変色率はそれ以上大きくならないので、２０時間以上紫外線を照射しても、無駄であることが分り、また（表５）から、金属被覆率が７．５％で変色率は１００％に達してしまうので、これ以上金属被覆率を増やしても無駄であり、金属被覆率は５％以下で十分といえる。

【００３５】（実施例８）先ず、（実施例１）と同様な方法で、二酸化チタン表面に銀、銅を担持した粒子懸濁液を作製した。出発塩としては硝酸銀、酢酸銅を用いた。この粒子懸濁液に水酸基を吸着する性質のある添加成分として、SiO_2、Al_2O_3を添加した。SiO_2、Al_2O_3は各々、日産化学社製シリカゾルスノーテックス、日産化学社製アルミナゾル５２０を用いた。懸濁液中の酸化チタンに対する金属の被覆率及びSiO_2、Al_2O_3の配合比を以下の（表６）に示すように調整し、タイル上に２．２×１０$^{-3}$g／cm^{2}だけ塗布し、８００℃で焼き付けてサンプルをえた。このサンプルの酸化分解力を抗菌性指標と油分解率により、また親水性を接触角にて（表６）に合せて示す。

【００３６】

【表６】

	金属/酸化チタン被覆率（%）	$SiO_2/Al_2O_3/TiO_2$配合比	油分解率（%）	抗菌力指標	親水性（水の接触角）	
					明時	暗時
①TiO_2	−	−	３０	１	１０	２７
②Cu/TiO_2	０．５	−	７０	１．５	１０	２５
③Ag/TiO_2	０．５	−	６５	２．５	１０	２７
④$TiO_2/Al_2O_3+SiO_2$	０．５	０．２/０．１/１	２５	１	３	２０
⑤$Cu/TiO_2+Al_2O_3+SiO_2$	０．５	０．２/０．１/１	６５	１．５	３	２０
⑥$Ag/TiO_2+Al_2O_3+SiO_2$	０．５	０．２/０．１/１	５５	２．５	３	２０
⑦$Ag/Cu/TiO_2+Al_2O_3+SiO_2$	Ag：０．２５ Cu：０．２５	０．２/０．１/１	７０	５．０	３	２０

水接触角測定方法…明時は紫外線強度１．２mw/cm^2 １２時間照射後測定、暗時は気乾状態の暗所にて１２時間放置後測定

①：酸化チタン単層コート品
②：銅前担持酸化チタンコート品
③：銀前担持酸化チタンコート品
④：アルミナ、シリカ添加酸化チタンコート品
⑤：アルミナ、シリカ添加銅前担持酸化チタンコート品
⑥：アルミナ、シリカ添加銀前担持酸化チタンコート品
⑦：アルミナ、シリカ添加銅、銀前担持酸化チタンコート品

【００３７】（表６）より、SiO_2、Al_2O_3を添加した金属前担持コーティングは酸化チタン単層と比較し、酸化分解力のみでなく親水性も向上することが分る。また、銀、銅を複合化した前担持系では、酸化分解力の向上が各成分のみを担持した時の単純な和ではなく、それ以上の向上を示している。

【００３８】SiO_2やAl_2O_3は光触媒である酸化チタンと同程度の湿潤熱を有する化合物である。湿潤熱は表面にＯＨ基が存在している物質ではその表面のＯＨ基を保持する特性を示す指標として捉えることができる。したがって、これらを添加することによって、酸化チタンが生成したＯＨ基をより効果的且つ高密度で化学吸着し

て保持でき、超親水性を長期にわたり付与できる。酸化チタンの湿潤性はアナターゼ型の場合は３２０～５１２$\times 10^{-3}$ J／m^2、ルチル型の場合は２９３～６４５$\times 10^{-3}$ J／m^2であることから、５００$\times 10^{-3}$ J／m^2程度の湿潤熱を有する化合物であることが好ましい。この条件を満たす化合物として、SiO_2、Al_2O_3、GeO_2、ThO_2、ZnO等が挙げられる。

【００３９】

【発明の効果】以上に説明した如く本発明に係る光触媒作用を有する機能材によれば、光触媒活性を助長する金属または金属化合物の微粒子が、光触媒活性点またはその近傍に担持されているので、光触媒活性の向上を図ることができる。

【００４０】また、本発明に係る光触媒作用を有する機能材の製造方法によれば、光触媒粒子の懸濁溶液中に光触媒活性を助長する金属を金属塩溶液の形態で添加して混合し、この混合が終了した後に、若しくは混合しつつ、混合溶液に紫外線を照射するようにしたので、光活性点若しくはその近傍に添加した金属またはその化合物を還元析出せしめることができる。

【００４１】更に、本発明に係る光触媒作用を有する複合機能材の製造方法によれば、前記の機能材を基材の表面に塗布した後、５００℃以上９００℃以下で加熱するだけで、複合機能材を得ることができる。

【図面の簡単な説明】

【図１】Cuの被覆率と硝酸銀呈色値との関係を示すグラフ

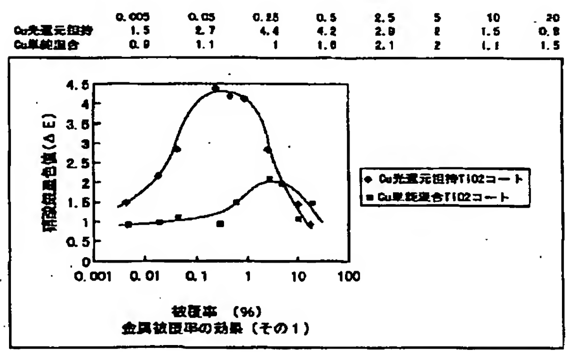
【図２】Cuの被覆率と油分解率との関係を示すグラフ

【図３】紫外線照射エネルギと硝酸銀呈色値との関係を示すグラフ

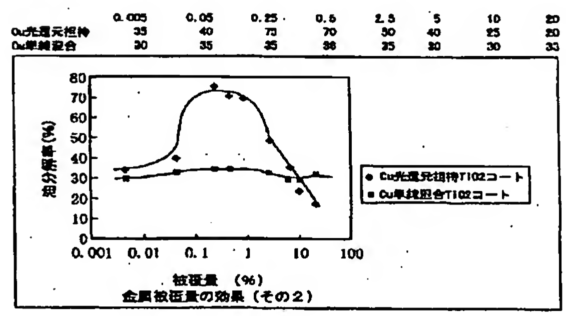
【図４】赤色染料（エオシンＹ）の分解実験装置の概略を示す図

【図５】紫外線の照射時間と変色率との関係を示すグラフ

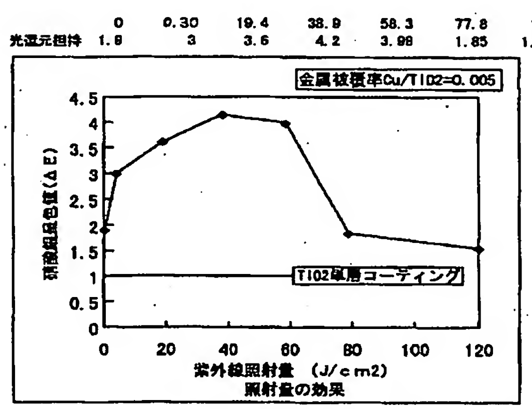
【図１】



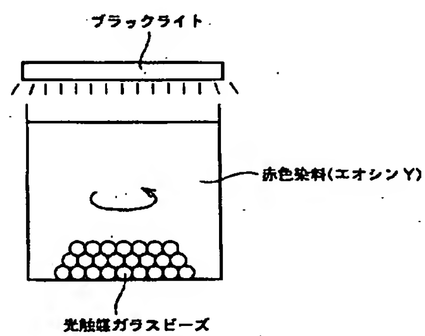
【図２】



【図３】



【図４】



【図5】

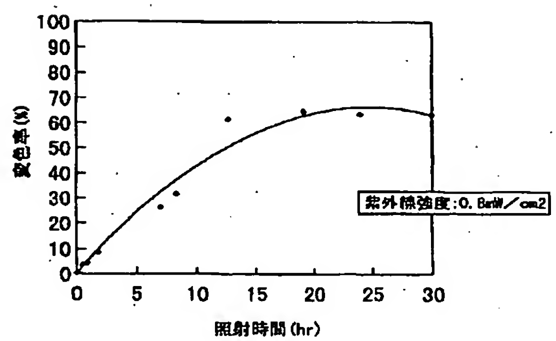


図1 変色率の経時変化

フロントページの続き

(51) Int. Cl.[6]		識別記号	F I		
B01J	23/12		B01J	23/12	M
	23/14			23/14	M
	23/38			23/38	M
	23/70			23/70	M
	27/04			27/04	M
	27/053			27/053	M
	27/14			27/14	M
C04B	41/86		C04B	41/86	A

Translation [machine] of JP 11-169726

CLAIMS

[Claim 1] It is the functional material which has the photocatalyst operation characterized by being the functional material which has the photocatalyst operation with which the metal or metallic compounds which promotes photocatalyst activity on the surface of a photocatalyst was supported, and said metal or metallic compounds being supported by the photocatalyst active spot or its near.

[Claim 2] The surface coverage with which the metal or metallic compounds which promotes the photocatalyst activity supported by the front face of said photocatalyst in the functional material which has a photocatalyst operation according to claim 1 covers a photocatalyst front face is functional material which has the photocatalyst operation characterized by being 5% or less.

[Claim 3] In the functional material which has a photocatalyst operation according to claim 1 or 2 said photocatalyst The metal or metallic compounds which is at least one of TiO2, SrTiO3, ZnO, SiC, GaP, CdS, CdSe, and MoS3 sorts, and promotes said photocatalyst activity Functional material which has the photocatalyst operation characterized by being at least one sort in Cu, Ag, nickel, Zn, Co, Fe, Pt, Pd, or these compounds.

[Claim 4] Functional material which is functional material which has a photocatalyst operation according to claim 1 to 3, and has the photocatalyst operation which a photocatalyst and an additive front face are made to carry out chemisorption of the hydroxyl group, and is characterized by demonstrating a hydrophilic property over a long period of time with the held hydroxyl group by adding a compound with the property which chemisorbs a hydroxyl group further.

[Claim 5] Functional material which has the photocatalyst operation characterized by being the functional material which has a photocatalyst operation according to claim 4, and said addition component being the compound which has the heat of wetting which said photocatalyst has, and the heat of wetting more than an EQC.

[Claim 6] Functional material which has the photocatalyst operation to which it is the functional material which has a photocatalyst operation according to claim 4, and said addition component considers as the description that they are at least one metallic compounds chosen from SiO2, aluminum 2O3, and GeO2, ThO2 and ZnO.

[Claim 7] After adding the metal which promotes photocatalyst activity with the gestalt of metal salting in liquid, mixing in the suspension solution of a photocatalyst particle and completing this mixing, by irradiating ultraviolet rays to a mixed solution The manufacture approach of the functional material which has the photocatalyst operation characterized by carrying out the reduction deposit of the metal which was made to produce an electron on the optical active spot of a photocatalyst particle, and was added to the optical active spot or its near with this electron, or its compound.

[Claim 8] the manufacture approach of the functional material which have the photocatalyst operation characterize by to carry out the reduction deposit of the metal which be made to produce an electron on the optical active spot of a photocatalyst particle , and be added to the optical active spot or its near with this electron by irradiate ultraviolet rays , add the metal which promote photocatalyst activity with the gestalt of metal salting in liquid , and mix in the suspension solution of a photocatalyst particle , or its compound .

[Claim 9] The manufacture approach of the functional material which has the photocatalyst operation characterized by making exposure energy (irradiation time x light source reinforcement) of the ultraviolet rays over said mixed solution or less [2 or more J //cm / 60] into two 0.3 J/cm in the manufacture approach of the functional material which has a photocatalyst operation according to claim 7 or 8.

[Claim 10] Compound functional material which has the photocatalyst operation characterized by preparing functional material according to claim 1 to 6 in a base material front face.

[Claim 11] Compound functional material which has the photocatalyst operation characterized by preparing said functional material in the base material front face through a binder in the compound functional material which has a photocatalyst operation according to claim 10.

[Claim 12] Compound functional material which has the photocatalyst operation characterized by carrying out mixed distribution of said functional material into a binder in the compound functional material which has a photocatalyst operation according to claim 11.

[Claim 13] It is the compound functional material which has the photocatalyst operation characterized by said binder being an inorganic compound or an organic compound in the compound functional material which has a photocatalyst operation according to claim 11.

[Claim 14] Compound functional material which has the photocatalyst operation characterized by said base material being a pottery product in the compound functional material which has a photocatalyst operation according to claim 10 to 13.

[Claim 15] Compound functional material which has the photocatalyst operation characterized by said base material being glass in the compound functional material which has a photocatalyst operation according to claim 10 to 13.

[Claim 16] claim 7 -- or -- or the manufacture approach of the compound functional material which has the photocatalyst operation characterized by heating below 500 degrees C or more 900 degrees C after manufacturing functional material and applying this functional material on the surface of a base material by the manufacture approach of the functional material indicated to claim 8.

[Claim 17] claim 7 -- or -- or the manufacture approach of the compound functional material which has the photocatalyst operation characterized by heating below 500 degrees C or more 900 degrees C after manufacturing functional material by the manufacture approach of the functional material indicated to claim 8, and applying a binder on the surface of a base material and applying

said functional material on this binder.

[Claim 18] claim 7 -- or -- or the manufacture approach of the compound functional material which has the photocatalyst operation characterized by applying to the front face of a base material and heating below 70 degrees C or more 150 degrees C after that further after manufacturing functional material and distributing this functional material in a binder by the manufacture approach of the functional material indicated to claim 8.

DETAILED DESCRIPTION

[0001]
[Field of the Invention] This invention relates to the functional material which has a photocatalyst operation, its manufacture approach and the compound functional material in which this functional material was formed on the front face, and its manufacture approach.
[0002]
[Description of the Prior Art] If ultraviolet rays are irradiated at photocatalysts, such as TiO2, an electron and an electron hole are produced and it is known from the former that the reaction in which these participate will occur. Furthermore, it turns out that photocatalyst activity improves by making a photocatalyst particle support the particle of transition metals or noble metals with recently.
[0003] And the approach indicated by the following official reports is learned as an approach of making a photocatalyst particle supporting the particle of noble metals etc. That is, the method of making the titania prepared with the hydrothermal crystallization method support noble metals by baking is indicated by JP,8-243390,A. Moreover, JP,8-283022,A carries out heating fusion of the Ti raw material containing metals, such as Pt, and manufacturing the compound particle which ultra-fine particles, such as Pt, projected on the particle front face of the anatase mold TiO2 and the rutile mold TiO2 by making the raw material which evaporated react with oxygen is indicated. Moreover, JP,8-283023,A carries out heating fusion of the Ti raw material containing metals, such as Pt, in the inert gas ambient atmosphere containing hydrogen gas, the ultrafine particle which consists of metals, such as Ti and Pt, is generated, and manufacturing the compound particle which metals, such as Pt, or the oxide of those distributed to homogeneity by heat-treating this ultrafine particle in atmospheric air further is indicated. Moreover, a titanium compound and a copper compound are dissolved in JP,9-132432,A into an organic solvent, and the approach of forming the coating film of amorphous structure by calcinating this solution is indicated.
[0004]
[Problem(s) to be Solved by the Invention] It is that ultraviolet rays etc. are irradiated, the electron (e-) which suited the valence band is excited by the conduction band, an electron hole (h+) produces an operation of a photocatalyst in a valence band, and it is thought that these electrons (e-) and an electron hole (h+) promote an oxidation reduction reaction etc. And by supporting the particle of noble metals, separation of the electron and electron hole which were generated is promoted and photocatalyst activity improves.
[0005] On the other hand, the active spot exists in a photocatalyst particle, and if improvement in

photocatalyst activity can be aimed at and a particle is supported with particles, such as noble metals, being supported by this active spot by parts other than the active spot, photocatalyst activity will be checked on the contrary. However, if it is in the conventional approach, each can select only the active spot and particles, such as noble metals, cannot be made to support.

[0006]

[Means for Solving the Problem] If the functional material which has the photocatalyst operation which relates to this invention that the above-mentioned technical problem should be solved was in claim 1, it is the functional material which has the photocatalyst operation with which the metal or metallic compounds which promotes photocatalyst activity on the surface of a photocatalyst was supported, and said metal or metallic compounds was considered as the configuration supported by the photocatalyst active spot or its near. Improvement in photocatalyst activity can be aimed at by considering as such a configuration. In addition, as a configuration of a photocatalyst, not only the shape of a particle but tabular, a porous body, etc. are arbitration.

[0007] Moreover, if the occupancy area to all the front faces of the metal which promotes photocatalyst activity, or metallic compounds is too large, the light absorption effectiveness of the photocatalyst active spot will fall, and photocatalyst activity will fall. Therefore, as for surface coverage, it is preferably desirable to consider as 1% or less 0.25% or more 5% or less.

[0008] Moreover, as said photocatalyst, at least one of TiO2, SrTiO3, ZnO, SiC, GaP, CdS, CdSe, and MoS3 sorts is mentioned, and at least one sort in Cu, Ag, nickel, Zn, Co, Fe, Pt, Pd, or these compounds is mentioned as said metal or metallic compounds.

[0009] Furthermore, the compound which has the property which chemisorbs a hydroxyl group as functional material which has a photocatalyst operation may be added. It becomes possible to demonstrate a hydrophilic property over a long period of time by doing in this way. The compound which has the heat of wetting which a photocatalyst has, and the heat of wetting more than an EQC as an addition component for this, for example, SiO2 and aluminum 2O3, GeO2, ThO2, ZnO, etc. are desirable.

[0010] Moreover, after the manufacture approach of the functional material which have the photocatalyst operation concerning this invention add the metal which promote photocatalyst activity with the gestalt of metal salting in liquid, and be mix in the suspension solution of a photocatalyst particle and this mixing be complete, it be irradiate ultraviolet rays at a mixed solution, an electron produce on the optical active spot of a photocatalyst particle, and the reduction deposit of the metal added to the optical active spot or its near with this electron or its compound carry out. Gestalten, such as a chloride, a nitrate, and a sulfate, can be considered as a metal salt.

[0011] Moreover, it be irradiate ultraviolet rays, the another manufacture approach of the functional material which have the photocatalyst operation concerning this invention add the metal which promote photocatalyst activity with the gestalt of metal salting in liquid, and be mix in the suspension solution of a photocatalyst particle, produce an electron on the optical active spot of a photocatalyst particle, and carry out the reduction deposit of the metal added to the optical active spot or its near with this electron, or its compound.

[0012] Thus, particles, such as noble metals, can be made to deposit only in the optical active spot or its near by using a photoreduction method.

[0013] Moreover, it is desirable to make it into two or less or more [0.3J //cm] 2 60 J/cm as exposure energy (irradiation time x light source reinforcement) of the ultraviolet rays over a mixed solution. If it separates from this range, activity will fall.

[0014] Moreover, the compound functional material which has the photocatalyst operation concerning this invention prepared the above mentioned functional material in the base material

front face. As a means to fix functional material to a base material front face, the binder which consists of an inorganic compound or an organic compound, for example is used. As a use mode of a binder, a binder is made to intervene between functional material and a base material front face, and also mixed distribution of the functional material may be carried out into a binder. Moreover, as a base material, a pottery product and glass are mentioned, for example.

[0015] Furthermore, after the manufacture approach of the compound functional material which has the photocatalyst operation concerning this invention manufactures functional material by the above mentioned approach first and applies this functional material on the surface of a base material, it is heated below 500 degrees C or more 900 degrees C. Moreover, before applying functional material on the surface of a base material, the binder is applied to the base material front face, and you may make it apply functional material to the front face of this binder. Furthermore, in carrying out mixed distribution of the functional material into a binder and applying this binder to a base material front face, after applying a binder to a base material front face, it heats at 70-150 degrees C.

[0016]

[Embodiment of the Invention] (Example 1) Optimum dose addition of the 0.5wt% water solution of a zinc chloride, ferric chloride (=), a nickel chloride, a copper chloride, and copper acetate was carried out at the Ishihara Sangyo titanium oxide sol (15% of STS-11:TiO_2 concentration). The amount of the added metal assumes that all the added metals deposited, and it was made for the titanium oxide particle coverage of a support metal to become about 0.5% at this time. Then, the above-mentioned water solution was diluted with tap water, it adjusted so that TiO_2 concentration might become 0.75%, and only 40 J/cm 2 irradiated ultraviolet rays, and TiO_2 front face was made to support a metal. And although the calcinated tile front face or the unglazed calcinated tile front face on which the solution which supported the metal on TiO_2 front face was given to the cover coat was coated with the frit which consists of a feldspar, potassium carbonate, etc., only 2.2x10-3 g/cm 3 was applied upwards, and it was able to be burned at 880 degrees C. The amount of coloration and oil solution engine performance of a silver nitrate estimated the photocatalyst activity of the obtained sample. Moreover, the baking film of the titanium oxide sol of (having no deposit by the photoreduction method) was produced as the metal was only mixed with the baking film of TiO_2 monolayer which does not add a metal as an example of a comparison, and same evaluation was carried out. A result is shown in the following (table 1).

[0017]

[Table 1]

[0018] From (Table 1), even if the film obtained by this invention approach is the case where which metal is added, TiO_2 monolayer is understood that photocatalyst activity is higher than the coat of Cu simple mixed stock from the first.

[0019] (Example 2) The effectiveness of the amount of support metals exerted on photocatalyst activity was investigated in the following experiments. First, Cu was made to support with the same approach as (an example 1) by making copper acetate into a start salt on a titanium oxide particle front face. However, the amount of support of Cu was changed in 0 - 20% of range by the coverage on the front face of a photocatalyst. The coloration value and oil solution engine performance of a silver nitrate estimated the photocatalyst activity of the obtained sample. Moreover, the simple hybrid model titanium oxide baking film which set the amount of addition metals constant was produced as an example of a comparison, and same evaluation was performed. A result is shown in drawing 1 and drawing 2 .

[0020] When coverage becomes 10% from drawing 1 and drawing 2 , and the coloration value and oil solution engine performance of a silver nitrate fall sharply, and especially coverage has good coloration value and oil solution engine performance of a silver nitrate in 0.25 - 1% of range and exceeds [which added Cu superfluously] this range, it turns out that the coloration value and oil solution engine performance of a silver nitrate deteriorate rapidly.
[0021] (Example 3) It experimented about the effect of the amount of exposure energy of the ultraviolet rays of the metal support process exerted on photocatalyst activity (irradiation time x light source reinforcement). First, Cu was made to support with the same approach as (an example 1) by making copper acetate into a start salt on a titanium oxide particle front face. However, the amount of energy of metal support was changed by 0 - 120 J/cm2. A result is shown in drawing 3 .
[0022] Drawing 3 shows that photocatalyst activity falls on the contrary, when exposure energy serves as 80 J/cm2. And as an amount of exposure energy of ultraviolet rays, it also turns out that 0.3 J/cm2 - 60 J/cm2 are suitable.
[0023] (Example 4) The experiment which gives photocatalyst activity to a base material front face by the photocatalyst particle which supported the metal was conducted. First, the copper acetate water solution (0.5wt%) was added to the Ishihara Sangyo titanium oxide sol (15% of STS-11:TiO2 concentration). In addition, having assumed that all the added metals deposited, the amount of the added metal was adjusted so that the titanium oxide particle coverage of a support metal might become about 0.5%. Then, dilute with tap water further and it is made for TiO2 concentration to become 0.75%, and only 40 J/cm 2 irradiated ultraviolet rays, stirring, and the TiO2 particle front face was made to support Cu. This was applied to the 7mm glass bead by the dipping method, it could be burned at 650 degrees C, and the photocatalyst bead was produced. The above-mentioned photocatalyst bead (diameter of 7mm) 80g was put in in the container, as shown in drawing 4 , and the red color (eosine Y: 2 ppm, 200ml) was decomposed. The trial with the same said of the glass bead which performed TiO2 monolayer coating which does not support a metal, and coating of a metaled simple hybrid model as an example of a comparison was performed. A result is shown in the following (table 2). In addition, the cracking severity in (Table 2) shows the decoloring condition of a color.
[0024]
[Table 2]

[0025] TiO2 coating which it deposited [coating] and made Cu support with a photoreduction method from (Table 2) shows high activity in decomposition of a red color.
[0026] (Example 5) First, Cu was made to support with the same approach as (an example 1) by having made copper acetate into the start salt on a titanium oxide particle front face, and silicone resin (Shin-etsu chemistry KP858) was mixed to this by it. And after setting the solid content ratio of titanium oxide and SHIRIKO resin to 7:3, AUW was diluted with ethanol 3 times and it considered as coating liquid. On the other hand, a base material carried out heat curing of the binder about 30 minutes at 150 degrees C, after applying coating liquid using a tile with a spin coating method (how to make rotate a substrate after coating liquid is dropped at a substrate, to diffuse with a centrifugal force, and form a uniform coat). The photocatalyst activity of the acquired sample object was evaluated to antibacterial. About the example of a comparison, it produced using the above-mentioned silicone resin binder using the titanium oxide sol of Cu simple hybrid model, and the titanium oxide single taste sol. A result is shown in the following (table 3).
[0027]
[Table 3]

[0028] Even when the functional material concerning this invention is mixed from (Table 3) to silicone resin, it turns out that photocatalyst activity improves.
[0029] (Example 6) The coating liquid which contains the titanium oxide particle which supported Cu, and the silicone resin as a binder by the same approach as an example 5 was prepared. On the other hand, a base material carried out heat curing of the binder about 30 minutes at 80 degrees C, after applying coating liquid by spin coating using the acrylic board beforehand coated with silicone resin. Antibacterial estimated the photocatalyst activity of the obtained specimen. About the example of a comparison, it produced using the above-mentioned silicone resin binder using the titanium oxide sol of Cu simple hybrid model, and the titanium oxide single taste sol. A result is shown in the following (table 4).
[0030]
[Table 4]

[0031] Even when the functional material concerning this invention is mixed from the (table 4) as well as (an example 5) to silicone resin, it turns out that photocatalyst activity improves.
[0032] (Example 7) It experimented about the discolour ratio. Here, they are the discolour ratio = discoloration color difference / saturation discoloration color difference. First, ultraviolet rays were irradiated while titanium oxide concentration added copper acetate to the sol which is 0.75%. Although the discoloration color difference increased when the copper quantity and UV irradiation to add increased, discoloration was reaching the ceiling (saturation) copper acetate / titanium oxide =15% in UV irradiation time amount 48 hours. The discoloration color difference at this time is made into the saturation discoloration color difference. Next, copper acetate was added, ultraviolet rays (0.8 mW/cm2) were irradiated so that copper titanium oxide coverage might become 0.5% to the sol whose titanium oxide concentration is 0.75%, and the discoloration color difference was searched for with time. And the result of having computed the discolour ratio is shown in drawing 5 . Moreover, to the sol whose titanium oxide concentration is 0.75%, copper acetate was added so that the rate of metallic coating might become 0.1 - 7.5%, ultraviolet rays (0.8 mW/cm2) were irradiated for 18 hours, and the relation between a discolour ratio and the rate of metallic coating was examined. A result is shown in the following (table 5).
[0033]
[Table 5]

[0034] first, being useless even if it irradiates ultraviolet rays for 20 hours or more, since a discolour ratio will not become large any more, if irradiation time exceeds 20 hours from drawing 5 -- understanding -- moreover (Table 5) -- from -- since a discolour ratio reaches to 100% at 7.5%, even if the rate of metallic coating increases the rate of metallic coating more than this -- useless -- the rate of metallic coating -- 5% or less -- enough -- ** -- it can say.
[0035] (Example 8) The particle suspension which supported silver and copper with the same approach as (an example 1) on the titanium-dioxide front face first was produced. A silver nitrate and copper acetate were used as a start salt. As an addition component which has the property to adsorb a hydroxyl group in this particle suspension, SiO2 and aluminum 2O3 were added. SiO2 and aluminum 2O3 used the silica sol snow tex by the Nissan chemistry company, and the alumina sol 520 by the Nissan chemistry company respectively. The metaled coverage to the titanium oxide

in suspension and the compounding ratio of SiO2 and aluminum 2O3 were adjusted as shown in the following (table 6), only 2.2x10-3 g/cm 2 was applied on the tile, it could be burned at 800 degrees C, and the sample was obtained. An antibacterial index and oil cracking severity show a hydrophilic property again according to a contact angle (Table 6) for the oxidative degradation force of this sample.
[0036]
[Table 6]

[0037] (Table 6) shows that support-before metal coating of a hydrophilic property [not only the oxidative degradation force but] which added SiO2 and aluminum 2O3 improves as compared with a titanium oxide monolayer. Moreover, the pre-support system which compound-ized silver and copper shows not the simple sum when improvement in the oxidative degradation force supports only each component but the improvement beyond it.
[0038] SiO2 and aluminum 2O3 are compounds which have the heat of wetting comparable as the titanium oxide which is a photocatalyst. The heat of wetting can be regarded as an index which shows the property of holding the OH radical of the front face by the matter by which the OH radical exists in the front face. Therefore, by adding these, it can be more effective and high-density, the OH radical which titanium oxide generated can be chemisorbed and held, and a super-hydrophilic property can be given over a long period of time. In the case of an anatase mold, since it is 293 - 645x10-3 J/m2 in the case of 320 - 512x10-3 J/m2 and a rutile mold, as for the wettability of titanium oxide, it is desirable that it is the compound which has the about two 500x10-3 J/m heat of wetting. As a compound which fulfills this condition, SiO2, aluminum 2O3, GeO2, ThO2, ZnO, etc. are mentioned.
[0039]
[Effect of the Invention] According to the functional material which has the photocatalyst operation which relates to this invention as explained above, since the particle of the metal which promotes photocatalyst activity, or metallic compounds is supported by the photocatalyst active spot or its near, it can aim at improvement in photocatalyst activity.
[0040] Moreover, since it was made irradiate ultraviolet rays at a mixed solution, mixing according to the manufacture approach of the functional material which has the photocatalyst operation concerning this invention after adding the metal which promotes photocatalyst activity with the gestalt of metal salting in liquid, mixing in the suspension solution of a photocatalyst particle and completing this mixing, the reduction deposit of the metal added to the optical active spot or its near or its compound is carried out.
[0041] Furthermore, according to the manufacture approach of the compound functional material which has the photocatalyst operation concerning this invention, after applying the aforementioned functional material on the surface of a base material, compound functional material can be obtained only by heating below 500 degrees C or more 900 degrees C.

Translation [machine] of JP 2000-038686

CLAIMS

[Claim 1] It is the metal plate which the photocatalyst particle layer is formed on the surface of the metal plate, and was excellent in light catalytic and workability which are formed when this photocatalyst particle layer calcinates the titanium oxide particle in which the discontinuity coat with a major axis of 0.1 micrometers or less which consists of the metal or alloy which promotes the photocatalyst activity of titanium oxide is formed in 1 - 20% of the weight of the amount of covering at the temperature of 140-700 degrees C to a metal plate.

[Claim 2] The metal plate of claim 1 with which the metal or alloy which promotes light catalytic includes at least one kind in a ruthenium, gold, platinum, chromium, silver, copper, zinc, and nickel.

[Claim 3] The metal plate according to claim 1 or 2 whose concavo-convex difference of a photocatalyst particle layer is 500 micrometers or less.

DETAILED DESCRIPTION

[0001]
[Industrial Application] This invention is suitable for disassembly of the oil adhering to a cooking appliance etc., dirt decomposition of a sheathing material, deordorization, environmental purification, carbon-dioxide immobilization, etc., and relates to the metal plate excellent in a photocatalyst function and workability.
[0002]
[Description of the Prior Art] The photocatalyst approach which disassembles an oil into the titanium oxide applied to the heat catalyst approach of heating an oil to this catalyst and coincidence as an approach of disassembling the oil adhering to a cooking appliance etc., using manganese oxide as a catalyst, and promoting the perfect combustion of an oil, a steel plate, a filter, etc. by irradiating ultraviolet rays is adopted. Especially, the photocatalyst method has been used for various fields, such as immobilization of decomposition of not only an oil solution but NOX (nitrogen oxides) and SOX (sulfur oxide), disassembly of organic system dirt, antibacterial, and a carbon dioxide.
[0003]
[Problem(s) to be Solved by the Invention] Since it is not necessary to hold a photocatalyst to an elevated temperature as compared with a heat catalyst, need is increasing quickly. However, since the inorganic system catalyst represented by titanium oxide is begun by UV irradiation and a catalysis is made to discover, the attachment of an ultraviolet ray lamp is needed. UV irradiation has a possibility of having a bad influence also on the body, and the cure which prevents the

leakage to the exterior of ultraviolet rays is also needed. There is an organic semiconductive polymer as matter excited on the wavelength comparatively near a light region. However, an organic semiconductive polymer does not have a catalysis as strong as it can disassemble an oil and dirt, and has many troubles in utilization.

[0004] If the ion implantation of the transition metals, such as chromium, is carried out to titanium oxide, presenting a photocatalyst operation in a light region is also reported [Yuichi Ichihashi, a catalyst, and 39(2) 146 (1997)]. However, many problems that a manufacturing cost is high when based on an ion implantation, and it is unsolved for using it in a practically extensive field are left behind. The particle in which the discontinuity coat of specific covering material was formed on the front face of a titanium oxide particle with a particle size of 1 micrometer or less found out excelling before in photocatalyst activity also in the light of long wavelength, and the basis of such a background, this invention person, etc. applied as Japanese Patent Application No. No. 182270 [ten to]. If there is the metal or alloy of a ruthenium, gold, platinum, and chromium as covering material and this is covered with powder sputtering, nonelectrolytic plating, etc. on the front face of a titanium oxide particle, also in a long wavelength field, catalytic activity will be discovered.

[0005]

[Means for Solving the Problem] This invention raises the adhesion over a co-catalyst-operation and titanium oxide particle of the quality of a coating, and aims at offering the metal plate which has also improved workability while it secures the exposure surface area of a titanium oxide particle by being developed that the property of the covering titanium oxide particle proposed previously should be utilized further, and making an enveloping layer condense using baking at the time of the ability of a covering titanium oxide particle to be burned on a metal plate front face. In order that this invention may attain the purpose, the photocatalyst particle layer is formed on the surface of the metal plate, and this photocatalyst particle layer is characterized by being formed by calcinating the titanium oxide particle in which it becomes from the metal or alloy which promotes the photocatalyst activity of titanium oxide, and the discontinuity coat with a major axis of 0.1 micrometers or less is formed in 1 - 20% of the weight of the amount of covering at the temperature of 140-700 degrees C to a metal plate. As the metal which promotes light catalytic, or an alloy, a metal or alloy including at least one kind in a ruthenium, gold, platinum, chromium, silver, copper, zinc, and nickel is used. As for the photocatalyst particle layer formed on the surface of a metal plate, it is desirable to have a concavo-convex difference 500 micrometers or less.

[0006]

[Embodiment of the Invention] The metal plate of this invention has given photocatalyst ability by forming the photocatalyst particle layer which consists of a titanium oxide particle in which discontinuity coats, such as a ruthenium, gold, platinum, chromium, silver, copper, zinc, and nickel, were formed on front faces, such as a steel plate, a stainless steel plate, a surface treated steel sheet, a chemical conversion steel plate, and an aluminum plate. As a titanium oxide particle, although the point of photocatalyst activity to an anatase mold is desirable, especially particle shape is not restrained. However, when acquiring the quantum size effect which promotes a photocatalysis, a titanium oxide particle 1 micrometer or less has a desirable mean diameter. In using as a raw material the titanium oxide particle condensed remarkably, it uses it, cracking suitably. As shown in <u>drawing 1</u> , the discontinuity coat 2 is formed in the front face of the titanium oxide particle 1. The discontinuity coat 2 consists of the metal or alloy containing at least one sort of a ruthenium, gold, platinum, chromium, silver, copper, zinc, and nickel, or two sorts or more.

[0007] As for the titanium oxide particle 1 covered by the discontinuity coat 2, a long wavelength side also comes to present a photocatalyst operation rather than an ultraviolet region. The manifestation of a photocatalyst operation is imagined to be what is depended on the following

reason. As for a metal or alloys, such as a ruthenium, gold, platinum, chromium, silver, copper, zinc, and nickel, the scaling object has a semi-conductor property. For example, with the silver with which the front face was covered by the silver oxide, as compared with band gap 3.2eV of titanium oxide, it is very as narrow as 1.2eV, and the band gap in a room temperature is easily excited by the exposure of a light of wavelength shorter than a light region or it, and produces an electron and an electron hole by it.

[0008] Since the discontinuity coat in which the titanium oxide of a base material is a particle and has a semi-conductor property at this time is formed in the particle front face, the electron and electron hole which were generated become a reactant high thing, without receiving thermal relaxation with a grid according to a quantum size effect. A part of electron generated and emitted by the optical exposure and electron hole are supplied to the titanium oxide of a base material through a coat. On the other hand, the electron and electron hole which were generated on the surface of titanium oxide by excitation by the ultraviolet rays included in the lights, such as sunlight, exist. The electron supplied from the coat and an electron hole make the photocatalyst activity of titanium oxide increase in collaboration with the electron and electron hole in a titanium oxide front face. Consequently, even if it omits or mitigates UV irradiation, a photocatalysis effective in organic substance disassembly of an oil, dirt, etc. advances.

[0009] The catalysis which oxidizes the organic substance also in itself occurs, and a ruthenium, gold, platinum, chromium, silver, copper, zinc, nickel, etc. are [the catalytic activity of titanium oxide, and] SOX and NOX conjointly. It works also to decomposition or oxidization of the organic substance. However, if an enveloping layer is formed all over a titanium oxide particle, a photocatalyst operation of titanium oxide original will not be discovered. Then, if it is in this invention, coating weight is regulated to 1 - 20% of the weight like point **, and the discontinuity coats 1, such as the shape of the shape of an island, punctiform, and a muscle, are formed for the enveloping layer (drawing 1). The amount of covering which is not filled to 1% of the weight is not enough as the effectiveness in which the discontinuity coat was formed. On the other hand, covering cost not only becomes high, but in the amount of covering exceeding 20 % of the weight, the whole surface of the titanium oxide particle 2 is covered by the discontinuity coat 1, and the photocatalyst activity of titanium oxide is spoiled.

[0010] The discontinuity coat 2 needs to distribute on the front face of the titanium oxide particle 1 in size with a major axis of 0.1 micrometers or less. According to detailed-izing of the discontinuity coat 2, the surface area of the titanium oxide particle 1 and the discontinuity coat 2 increases, and the catalytic activity which oxidizes the organic substance etc. improves. If the major axis of the discontinuity coat 2 is especially set to 0.1 micrometers or less, the quantum size effect which promotes migration of an electron and an electron hole will show up, and catalytic activity will improve notably. The powder sputtering method which these people introduced by JP,2-153068,A is suitable for formation of a discontinuity coat. Although a discontinuity coat is formed also with nonelectrolytic plating, it is also required that it should control plating conditions strictly that the metal layer which deposits with nonelectrolytic plating covers the whole surface of a titanium oxide particle for a certain reason.

[0011] It is NOX, when applying a covering titanium oxide particle to a metal plate front face and forming the stratum functionale in a metal plate front face. In order to make a photocatalyst operation of decomposition etc. discover, it is important to consider as the stratum functionale which the front face of a titanium oxide particle exposed. As such a covering approach, there are a spray method, a dip method, a sol gel process, physical vapor deposition, a powder coating method, etc. Especially, according to the spray method, as shown in drawing 2 , the photocatalyst particle layer 3 with big irregularity is formed in the front face of a metal plate 4. Since the irregular

photocatalyst particle layer 3 has big surface area, a photocatalysis is promoted. However, if there is too big concavo-convex difference deltaH, the workability of the metal plate 4 which formed the photocatalyst particle layer 3 will worsen, a crack will occur in the photocatalyst particle layer 3 in the cases, such as press working of sheet metal, and a photocatalyst particle will dedrop come to be easy from a metal plate 4. According to the research studies, such as this invention person, when holding down concavo-convex difference deltaH to 500 micrometers or less, it turned out that omission of a photocatalyst particle are controlled, it originates in the increment in surface area, and photocatalyst ability improves. Moreover, in spray painting, since it can paint only using an volatile high organic solvent, without making resin etc. distribute a titanium oxide particle, paint costs are also mitigated.

[0012] In order that the photocatalyst particle layer 3 formed in the front face of a metal plate 4 may remove a solvent after paint, heat treatment for 10 minutes or more is performed at 140-700 degrees C. By this heat treatment, the metal or alloy which constitutes the discontinuity coat 2 works as a kind of binder, and the adhesion of the photocatalyst particle layer 3 to a metal plate 4 improves. Moreover, the discontinuity coat 2 formed in the front face of the titanium oxide particle 1 is also condensed moderately, and the exposure surface area of the titanium oxide particle 1 is secured. In short-time baking which does not reach in the burning temperature of less than 140 degrees C, or 10 minutes, some solvents remain between covering titanium oxide particles, and sufficient photocatalyst property may not be discovered. The bond strength of perfect removal and the titanium oxide of a solvent, and a covering metal improves, so that burning temperature becomes high. However, it is not desirable from the structure of a titanium oxide particle metamorphosing into a rutile mold from an anatase mold in the burning temperature exceeding 700 degrees C. Moreover, burning temperature is set up lower than the melting point of the metal which constitutes the discontinuity coat currently formed in the front face of a titanium oxide particle, or an alloy. In the heat treatment temperature exceeding the melting point, a discontinuity coat condenses mutually, and in order to make it big and rough, there is a possibility that the gap between each titanium oxide particles 2 may be filled up with the metal or alloy of a coat, or the adhesion of a titanium oxide particle may fall.

[0013] On the other hand, if it calcinates at the temperature below the melting point, while the counter diffusion of the discontinuity coat 1 will be suppressed moderately and the proper exposure surface area of the titanium oxide particle 2 will be secured, the adhesion of the discontinuity coat 1 to the titanium oxide particle 2 improves. Consequently, the workability of the metal plate 4 with which the photocatalyst particle layer 3 was formed also improves. thus, the metal plate with which the photocatalyst particle layer 3 was formed -- the conventional ultraviolet-rays wavelength region -- setting -- NOX and SOX etc. -- decomposing -- the effectiveness of environmental purification -- raising -- the long wave of a light region -- Nagamitsu -- also setting -- NOX The dirt of an organic substance system can be disassembled. And since it excels in workability, it can be processed into various products and used in an extensive field.

[0014]

[Example] Various metals or alloys which promote photocatalyst activity were covered with the 10 % of the weight of the amounts of covering to the titanium oxide powder of 0.5 micrometers of mean diameters using the [example 1] magnetron mold sputtering system (output of 10kW). Covering powder was distributed to the mixed solvent of butyl Cellosolve and a 2-propanol, and it painted to the galvanized steel sheet of 0.65mm of board thickness using the spray gun, and at 200 degrees C, it could be burned for 20 minutes and carried out. In addition, as a galvanized steel sheet, in order to improve the adhesion of titanium oxide powder, what formed the silica coat with the spray method beforehand was used. The quantity for application of covering powder was

adjusted so that the average thickness of the photocatalyst particle layer 3 formed on the surface of a galvanized steel sheet might be set to 5-105 micrometers. The formed photocatalyst particle layer 3 had 5 micrometers in the crevice, and had the thickness of 105 micrometers by heights, and concavo-convex difference deltaH was 100 micrometers.

[0015] About the obtained metal plate, it is NOX with the following approach. The decomposition property was investigated. The 100mmx100mm test piece was cut down from the metal plate with which the photocatalyst particle layer was formed, and it put into what carried out series connection of the glass reactor (it is 25mm in thickness at the diameter of 160mm) of a petri dish mold. And 1 ppm NOX NOX [in / while passing the purification air to include, a near ultraviolet ray with a wavelength of 300-400nm is irradiated from the outside of a reactor using the black light for photochemistries (Toshiba Corp. make H100BL, 100W), and / a reactor outlet] 24 timing measurement of the concentration was carried out. The photocatalyst ability of each metal plate was judged based on measured value. In addition, evaluation of a decomposition property is NOX obtained by the approach same about the metal plate (comparison material) which carried out spray painting of the titanium oxide independent particle of the same particle size. Made the decomposition property into the reference value, what exceeds 0.8 times for what exceeds 1.0 times for the thing exceeding the twice of a reference value by O and 2 double less or equal by O and 1.0 or less times was made into **, and 0.8 or less times was made into x.

[0016] The metal plate which prepared the photocatalyst particle layer according to this invention so that the results of an investigation of Table 1 and 2 might see is NOX [compare with the metal plate in which the titanium oxide independent paint film was formed, and] under UV irradiation. It turns out that it excels in the decomposition property. Moreover, the light source is replaced with the positive glow lamp (Toshiba Corp. make D125,125W) which carries out outgoing radiation of the light with the wavelength of an infrared-radiation - light region, and it is NOX similarly. The decomposition property was evaluated. The result is combined and shown in Table 1 and 2. In a positive glow exposure, it is NOX with low non-covered titanium oxide. NOX high at the titanium oxide which carried out covering processing to only resolving power being shown according to this invention The effectiveness of covering, such as a ruthenium, gold, platinum, and chromium, is checked by that resolving power is obtained. However, NOX according to covering at that by which the amount of covering exceeds less than 1 % of the weight or 20 % of the weight even if it is the titanium oxide particle which covered a ruthenium, gold, platinum, and chromium The improvement of resolution was not found.

[0017]

表1：被覆層の種類がNO_x分解能に及ぼす影響

被覆物質	被覆方法	被覆量重量%	NO_x分解能		区分
			紫外線照射	陽光照射	
Ag	無電解めっき	1	○	○	本発明例
		10	○	○	
		20	○	○	
	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	○	◎	
		25	×	×	比較例
Cu	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	○	◎	
		25	×	×	比較例
Zn	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	○	○	
		25	×	×	比較例
Ni	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	○	○	
		25	×	×	比較例
無被覆の酸化チタン粉末			△	×	参照例

[0018]

表2：被覆層の種類がNO_x分解能に及ぼす影響

被覆物質	被覆方法	被覆量 重量%	NO_x分解能		区分
			紫外線照射	陽光照射	
Ru	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	◎	◎	
		25	×	×	比較例
Au	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	○	○	
		25	×	×	比較例
Cr	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	◎	◎	
		25	×	×	比較例
Pt	物理蒸着	0.5	△	△	比較例
		1	○	○	本発明例
		10	◎	◎	
		20	◎	◎	
		25	×	×	比較例

[0019] Furthermore Ag-30-% of the weight Cu, Ag-30-% of the weight Zn, Ag-30-% of the weight nickel, Cu-30-% of the weight Ag, Cu-30-% of the weight Zn, Cu-30-% of the weight nickel, Zn-30-% of the weight Ag, Zn-30-% of the weight Cu, Zn-30-% of the weight nickel, and nickel-30-% of the weight Ag, nickel-30 % of the weight Cu, nickel-30-% of the weight Zn, Ru-30-% of the weight Au, Ru-30-% of the weight Pt, Ru-30 % of the weight Cr, Au-30-% of the weight Ru, Au-30 % of the weight Pt, Au-30 % of the weight Cr, Pt-30-% of the weight Ru, Pt-30 % of the weight Au, Pt-30 % of the weight Cr, and Cr-30-% of the weight Ru, Cr-30 % of the weight Au, Cr-30-% of the weight Pt, Ag-20-% of the weight Cu-20-% of the weight Zn, Ag-20-% of the weight Cu-20-% of the weight nickel, Ag-20-% of the weight Zn-20-% of the weight nickel, Ru-20-% of the weight Au-20-% of the weight Pt, Ru-20 % of the weight Au-20 % of the weight Cr, Alloys, such as Ru-20 % of the weight Pt-20 % of the weight Cr, covered the titanium oxide particle of 0.5 micrometers of mean diameters at the 10 % of the weight of the amounts of covering. The titanium oxide particle which covered the titanium oxide particle in which these alloy coat was formed is used, and it is NOX similarly. NOX which excelled in any [of UV irradiation and a positive glow exposure] case when resolution was investigated Resolution was shown.

[0020] Subsequently, from the metal plate with which the photocatalyst particle layer was formed, the test piece with a width of face [of 50mm] and a die length of 120mm was cut down, and the bending test was presented 90 degrees using the shaft of the shape of a cylinder with a diameter of 8mm. And the photocatalyst particle layer of the processing section was observed and the existence of a crack was investigated. Consequently, a crack was not detected in what prepared the photocatalyst particle layer using the titanium oxide with which the discontinuity coat of a metal or an alloy was formed to the crack having been detected in the thing in which the photocatalyst

particle layer was formed according to this invention by the titanium oxide independent. It turns out that the metal plate which prepared the photocatalyst particle layer according to this invention is excellent also in workability so that clearly from this contrast.

[0021] [Example 2] The powder which covered Zn and Ru-50 % of the weight Pt with the sputtering method 5% of the weight Ag-50% of the weight, respectively was produced using the titanium oxide particle which has various mean diameters. Two kinds of alloy plate titanium oxide is used as a metal plate front face with ** with a spray method, and the mean particle diameter of a titanium oxide particle is NOX. The effect affect resolution was investigated by the same approach as an example 1. Consequently, alloy plate titanium oxide with a particle size of 1 micrometer or less is NOX superior to a titanium oxide independent. Resolution was shown. Especially at the thing for which particle size used the titanium oxide particle 0.5 micrometers or less, it is NOX. The high value to which the amount of decomposition exceeds twice was shown. On the other hand, in what gave the alloy plate to the titanium oxide particle to which particle size exceeds 1 micrometer, even if compared with the titanium oxide independent thing, the property was inferior.

[0022] The powder which therefore covered Ag-50 % of the weight Cu and Ru-50 % of the weight Au 10% of the weight by the sputtering method, respectively was produced using the titanium oxide particle of 0.1 micrometers of [example 3] mean diameters. Two kinds of alloy plate titanium oxide was used as the metal plate with ** with the spray method, and the photocatalyst particle layer was formed. It had become the front face on which the obtained photocatalyst particle layer has 5 micrometers in a crevice, and has the irregularity of 7-705 micrometers by heights, and concavo-convex difference deltaH was 2-700 micrometers. NOX of each metal plate Resolving power is measured like an example 1 and it is NOX. The effect of the concavo-convex difference delta H exerted on resolving power was investigated. Moreover, it investigated also about the existence of the crack of the titanium oxide coat in the processing section.

[0023] Consequently, at that in which the irregular photocatalyst particle layer was formed, it is NOX. Compared with the titanium oxide independent thing, it was all twice [more than] the resolving power of this. In the case of concavo-convex difference deltaH=10-500micrometer, it is NOX of 5 times or more especially. Resolution was shown and it has been grasped that concavo-convex difference deltaH has contributed to the decomposition property. However, the crack was observed by the photocatalyst particle layer of the processing section when concavo-convex difference deltaH exceeded 700 micrometers. NOX good from this In order to obtain resolution, the photocatalyst particle layer which attached big concavo-convex difference deltaH is desirable, but since workability is secured, irregularity difference [of 10-500 micrometers] deltaH can say that it is desirable. Concavo-convex difference deltaH is NOX. The effect affect improvement in resolution was the same even when other metals or the discontinuity coat of an alloy was formed.

[0024] In case the discontinuity coat of Zn and Ru-50 % of the weight Cr was formed in the titanium oxide particle of 0.3 micrometers of [example 4] mean diameters by the sputtering method Ag-20% of the weight, the amount of covering was changed in 0.5 - 22% of the weight of the range. The obtained alloy plate titanium oxide is used as a metal plate with spray method **, a photocatalyst particle layer is formed, and it is NOX. Resolution is measured by the same approach as an example 1, and it is NOX. The effect of the amount of covering exerted on resolution was investigated. Consequently, the titanium oxide particle which formed the discontinuity coat in the range of the 1 - 20 % of the weight of the amounts of covering is NOX which was excellent compared with the titanium oxide independent thing. Resolution is shown and it is twice [more than] as many NOX as this in the 3 - 10 % of the weight of especially the amounts of covering. Resolution was obtained. On the other hand, it compares with a titanium oxide independent particle in what formed the discontinuity coat at the 0.5 % of the weight of the amounts of covering, and 22

% of the weight, and is 0.8 to 1.0 times as many NOX as this. It had stopped at resolution being shown.
[0025] Zn and Ru-25 % of the weight Au-25 % of the weight Pt were covered with the sputtering method 20% of the weight using the titanium oxide particle of 1 micrometer of [example 5] mean diameters Ag-25-% of the weight Cu-25% of the weight. An electrical potential difference, a current, barrel rotational speed, agitating speed, etc. were changed at the time of sputtering, and the magnitude of the discontinuity coat formed in a titanium oxide particle front face was changed.. Each obtained alloy plate titanium oxide particle was used as the metal plate with ** with the spray method, and the photocatalyst particle layer was formed. It is NOX like [metal plate / with which the photocatalyst particle layer was formed] an example 1. Resolution is measured and the magnitude of a discontinuity coat is NOX. The effect affect resolution was investigated. Consequently, in the photocatalyst particle layer in which the discontinuity coat with the magnitude of 0.1 micrometers or less was made from the major axis from what was formed in the front face of a titanium oxide particle, it is twice [more than] as many NOX as this to a titanium oxide independent. Resolution was shown.
[0026] Ag-30 % of the weight Cu (melting point of 780 degrees C) and Ru-30 % of the weight Au (melting point of 2012 degrees C) were covered with the sputtering method 5% of the weight, respectively to the titanium oxide particle of 1 micrometer of [example 6] mean diameters. Each alloy plate titanium oxide particle was used as the metal plate with ** with the spray method, and it was able to be burned with various burning temperature for 10 minutes. Ten test pieces were cut down, respectively from each metal plate with which the alloy plate titanium oxide particle was calcinated, and workability was investigated by the bending test the 90 same degrees as an example 1. Collectively, it is NOX. Resolution was also investigated. This example estimated workability by the number of the test piece which the crack generated among all test pieces. By what was calcinated in the 140-700-degree C temperature requirement, the crack generating number was very small, and the photocatalyst particle layer had adhered to the metal plate in good adhesion, and showed good workability so that the results of an investigation of Table 3 might see. On the other hand, the crack was observed by most test pieces when burning temperature was less than 140 degrees C. Moreover, at what was calcinated at the temperature exceeding 700 degrees C, it is NOX. The fall of resolution was seen. NOX The fall of resolving power is imagined to be what has a cause in that some titanium oxide changed with high burning temperature to rutile type structure, and the discontinuity coat in the front face of a titanium oxide particle having condensed too much.
[0027]

表3：加工性及びNO$_x$分解能に及ぼす焼成温度の影響

焼成温度 ℃	Ag−30重量%Cu被覆		Ru−30重量%Au被覆		区分
	割れ個数	NO$_x$分解能	割れ個数	NO$_x$分解能	
130	8	◎	7	◎	比較例
140	1	◎	1	◎	本発明例
150	1	◎	1	◎	〃
300	0	◎	0	◎	〃
500	0	◎	0	◎	〃
650	1	◎	0	◎	〃
700	1	◎	1	◎	〃
750	1	△	1	△	比較例

[0028]
[Effect of the Invention] As explained above, this invention calcinates the titanium oxide particle in which the scaling object formed the discontinuity coat of the metal in which a semi-conductor property is shown, or an alloy under specific temperature conditions, and forms the photocatalyst particle layer in a metal plate front face. When positive glow including ultraviolet rays is irradiated as well as the bottom of UV irradiation, even if there is this photocatalyst particle layer, it presents the photocatalyst operation which disassembles NOX, SOX, and organic substance system dirt. And workability is also good. Therefore, various configurations, such as cookware, a kitchen instrument, a sheathing material, and interior material, can be processed, and it is used as a product with which the self-cleaning operation was given.

Translation of [machine] JP 2003-299965

CLAIMS

[Claim 1] the base for being fixed to the front face of photocatalyst ingredient support or the base currently fixed to the front face of photocatalyst ingredient support, and the photocatalyst crystalline of the shape of a column elongated from this base -- since -- the photocatalyst ingredient which is a becoming photocatalyst ingredient and is characterized by the noble-metals particle being supported by the front face of this photocatalyst ingredient.

[Claim 2] the base for being fixed to the front face of photocatalyst ingredient support or the base currently fixed to the front face of photocatalyst ingredient support, and the photocatalyst crystalline which takes the columnar structure of the hollow elongated from this base -- since -- the photocatalyst ingredient which is a becoming photocatalyst ingredient and is characterized by the noble-metals particle being supported by the front face of this photocatalyst ingredient.

[Claim 3] The photocatalyst ingredient according to claim 2 characterized by the structure which consists of a photocatalyst particle existing in the interior of said photocatalyst crystalline.

[Claim 4] When acetaldehyde gas is made to decompose using this photocatalyst ingredient that comes to use the photocatalyst of 0.1g of support **** supported on the photocatalyst ingredient support whose catalyst support area it is a photocatalyst ingredient according to claim 1 to 3, and is 75mmx75mm The photocatalyst ingredient characterized by the duration for setting acetaldehyde gas concentration in a glass container with a volume of 20l. to 1 ppm or less from 20 ppm being below for 5 minutes to 10 minutes.

[Claim 5] It is the photocatalyst ingredient according to claim 1 to 4 which said photocatalyst is titanium oxide, and said base is a crystalline nucleus, and is characterized by said noble metals being platinum.

[Claim 6] photocatalyst ingredient support and the photocatalyst ingredient according to claim 1 to 5 supported on this photocatalyst ingredient support -- since -- the becoming photocatalyst object.

[Claim 7] The original photocatalyst ingredient production process of obtaining the photocatalyst ingredient with which noble metals are not supported by the front face, It is the photocatalyst ingredient manufacture approach which consists of a noble-metals support process for supporting a noble-metals particle on the front face of the obtained original photocatalyst ingredient. This noble-metals support process The photocatalyst

ingredient manufacture approach characterized by including the adsorption process which is immersed in a noble-metals compound solution, adsorbs a noble-metals particle on a photocatalyst ingredient front face, and supports a photocatalyst ingredient, and the desiccation heat treatment process which noble metals dry the photocatalyst ingredient adsorbed and supported, and subsequently heat-treat.

[Claim 8] The photocatalyst ingredient manufacture approach according to claim 7 characterized by establishing the reduction process for returning the noble-metals particle of the oxidation state supported by said photocatalyst ingredient front face after said desiccation heat treatment process.

[Claim 9] The photocatalyst ingredient manufacture approach according to claim 7 or 8 characterized by being the compound with which said noble-metals compound contains platinum, such as hexa chloro (platinum VI) acid 6 hydrate.

[Claim 10] It is the photocatalyst ingredient manufacture approach which is the photocatalyst ingredient manufacture approach which serves as the original photocatalyst ingredient production process of obtaining the photocatalyst ingredient with which noble metals are not supported by the front face from a noble-metals support process in order to support noble metals on the front face of the obtained original photocatalyst ingredient, and is characterized by for this noble-metals support process to be a process which makes the front face of a original photocatalyst ingredient support a noble-metals particle with the sputtering method, a vacuum deposition method, or other physical vapor deposition.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] About a photocatalyst ingredient and its manufacture approach, in an oxide photocatalyst, especially this invention has the unique shape of crystal form and a unique surface structure, and relates to the oxide photocatalyst ingredient which can obtain the photocatalyst function of high activity, and its manufacture approach.
[0002]
[Description of the Prior Art] If the oxide photocatalyst represented by titanium oxide irradiates the light of wavelength with the energy more than the band gap, discovering a photocatalyst function by optical pumping is known from the former. The manifestation device of a photocatalyst function originates in producing an electron in a conduction band by optical pumping, and producing an electron hole in a valence band. By strong electronic reducing power and the strong oxidizing power of an electron hole, the organic substance and nitrogen oxides in contact with a photocatalyst are disassembled into water, carbon dioxide gas, etc., and it has antifouling, deodorization, an antibacterial function, etc.
[0003] Current attention of the environmental purification approach and equipment using antifouling of such an oxide photocatalyst, deodorization, and an antibacterial function is

carried out. That is, it originates in environmental pollution problems, such as water pollution of these days, and air pollution. In such a situation, in order to attain high-performance-izing and efficient-izing of the environmental purification approach, high activation of the photocatalyst function of the oxide photocatalyst itself is called for.

[0004] Since the oxide photocatalyst ingredient was usually powdered and it was used, handling was very difficult and it was difficult to include in an environmental purge. Since a powder-like oxide photocatalyst is fixed, a powder-like oxide photocatalyst is mixed with an organic binder, and it applies on a base material, and about it, it heats and there is the bottom of ordinary temperature or the approach of making it fix. However, in order that, as for this approach, the organic substance might cover most oxide photocatalyst most [parts or], the photocatalyst function had the fault of inactivating remarkably, compared with the powder itself. Since the organic binder which is the organic substance will furthermore be disassembled by the photocatalyst function, coat reinforcement deteriorates and there is another big problem concerning the endurance that powder will be omitted gradually. A photocatalyst function demonstrates a function only after a photocatalyst is exposed to a front face. Although the fault of powdered omission was conquered when a powder-like oxide photocatalyst was fixed with an inorganic binder, as for the problem that for a wrap reason the area of the effective front face for a photocatalyst functional manifestation will decrease, and a photocatalyst function will fall remarkably, a binder has not been improved in some oxide photocatalysts.

[0005] The production technique of many oxide photocatalysts is proposed until now [, such as a sol-gel method indicated by the sputtering method indicated by the vacuum deposition method indicated by JP,8-266910,A, JP,9-192498,A, etc., JP,8-309204,A, JP,11-12720,A, etc., JP,7-100378,A, JP,10-180118,A, etc. in order to solve the trouble of the above-mentioned powdered oxide photocatalyst]. Although solution of the trouble of an above-mentioned powdered oxide was tried by these advanced technology and the improvement of a photocatalyst function was achieved, the satisfactory thing was not obtained from the point of the high activation.

[0006] A photocatalyst function takes place as mentioned above in the photocatalyst body surface where light is irradiated. For this reason, the technique which controls the surface state of a photocatalyst object for the purpose of high activation of a photocatalyst function, or the technique which controls the crystal of a photocatalyst body surface layer is proposed from the former. A publication-number No. 57912 [nine to] official report, JP,10-36144,A, the publication-number No. 57817 [ten to] official report, and the publication-number No. 231146 [ten to] official report are indicated as a technique which controls the surface state of a photocatalyst object. The titanium oxide layer as a photocatalyst is formed in the front face of a glass substrate through the substrate film for direct or alkali cutoff, and the basic configuration indicated by these advanced technology forms silicon oxide in the front face of this titanium oxide layer.

[0007] By forming the silicon oxide film in porosity, or performing micro processing to the titanium oxide film or a glass substrate, each above-mentioned advanced technology is preparing irregularity on a front face, and is carrying out the work which raises a photocatalyst function.

[0008] That is, although it is said that the photocatalyst function improved when the area of the front face which a photocatalyst exposes by forming detailed irregularity in a front

face increases, remarkable improvement was not necessarily able to be attained. Moreover, processing of a substrate, processing of the film, insertion of a substrate layer, etc. had a problem also in respect of cost.

[0009] The publication number 2000-288403 is indicated as a technique which controls the crystal which constitutes a photocatalyst body surface layer. It is an anatase mold titanium oxide crystal, the configuration of 30% or more of crystal grain is an ellipse form or a half-ellipse form among the crystal grain of the titanium oxide which exists in the surface section, and the photocatalyst function of high activity is obtained by this by the basic configuration. Although the surface area to which a photocatalyst object exposes crystal grain by making it an ellipse form or a half-ellipse form increases and it is said that the photocatalyst function of this improved, remarkable improvement was not necessarily found.

[0010]

[Problem(s) to be Solved by the Invention] In the conventional technique mentioned above, although the improvement of the photocatalyst function that the oxide photocatalyst formed by controlling the crystal which constitutes control of the oxide photocatalyst formed by the various production approaches and a photocatalyst body surface condition and the surface layer section of a photocatalyst object is fixed is achieved, the oxide photocatalyst which has the photocatalyst function of further high activity is called for.

[0011] To the above-mentioned trouble, invention-in-this-application persons put the chief aim on high activation of the oxide photocatalyst by crystal form-like control, and considered wholeheartedly production of the oxide photocatalyst by the sol-gel method using various processes, such as chemical vapor deposition (henceforth a "CVD method"), and physical vapor deposition (henceforth "PVD"), and an organometallic compound, or inorganic metallic compounds. Consequently, the crystalline nucleus produced by various processes, such as a CVD method or PVD, was put in into the sol solution which consists of an organometallic compound or inorganic metallic compounds, or the sol solution was applied and heat-treated [solidified and] to this crystalline nucleus, and the approach of growing up a titanium oxide crystal from this crystalline nucleus was found out. And it traced that the photocatalyst function of high activity was obtained by considering as the crystal (henceforth a "pillar-shaped hollow crystal") of the pillar-shaped hollow structure where the shape of crystal form of the titanium oxide crystal grown up from this crystalline germ accomplishes a columnar crystal, and the interior of a crystal constitutes hollow structure. And it was based on this discovery, the new photocatalyst ingredient was invented and developed, and it indicated to the patent application (an application for patent 2001-058917, application for patent 2001-058918) of non-****.

[0012] <u>Drawing 6</u> is the mimetic diagram showing the appearance of the photocatalyst ingredient by the titanium oxide crystal which has the pillar-shaped hollow structure where it has developed [starting]. The base 52 to fix the developed photocatalyst ingredient 60 to the front face of the photocatalyst ingredient support 51 in drawing, It is mainly constituted. the photocatalyst crystalline 53 which takes the pillar-shaped hollow structure which is elongated from this base 52, and which is a columnar structure in the air -- since -- Are supported on the photocatalyst ingredient support 51, such as various kinds of substrates, such as fiber which has glass, a metal, the ceramics, or network

structure. It has the structure where the titanium oxide crystal 53 of pillar-shaped hollow structure is growing from the bases 52, such as a crystalline germ, (an application for patent 2001-058917, application for patent 2001-058918). Here, a column-like crystal is a generic name including all the configurations united as a prism, the shape of crystal form of cylindrical **, the shape of crystal form of the arborescence which branched, and two or more columnar crystals grew.

[0013] Since the obtained photocatalyst ingredient had fixed to the base material which is support, it was able to solve the problem of scattering like an end of complications-like photocatalyst. Moreover, the time amount which takes acetaldehyde gas with a concentration of 20 ppm to decrease 1 ppm or less became about 50% as compared with the powdered photocatalyst, acetaldehyde gas catabolic rate is high activity very much as a photocatalyst, such as doubling [about], and the thing very effective also in the utilization, such as an atmospheric-air purification system, was obtained.

[0014] However, in order to develop a photocatalyst technique further, to expand the applicable field and to develop it further, high activation of the further photocatalyst function is called for. That is, the technical problem which is going to solve this invention is offering the photocatalyst ingredient equipped with the photocatalyst function enduring the photocatalyst ingredient of the pillar-shaped hollow crystal which has high resolvability ability which invention-in-this-application persons' proposed previously, and its manufacture approach.

[0015]

[Means for Solving the Problem] Invention-in-this-application persons considered wholeheartedly high activation of the photocatalyst function by structure control of a pillar-shaped hollow crystal for the purpose of the further high activation of a photocatalyst function in the pillar-shaped hollow titanium oxide crystal in view of such a situation. Consequently, it came to complete a header and this invention for the photocatalyst function of further high activity being obtained by making the front face of a pillar-shaped hollow crystal support noble-metals particles, such as platinum. That is, the invention by which a patent claim is carried out by this application is as follows.

[0016] (1) the base for being fixed to the front face of photocatalyst ingredient support or the base currently fixed to the front face of photocatalyst ingredient support, and the photocatalyst crystalline of the shape of a column elongated from this base -- since -- the photocatalyst ingredient which is a becoming photocatalyst ingredient and is characterized by the noble-metals particle being supported by the front face of this photocatalyst ingredient.

[0017] (2) the base for being fixed to the front face of photocatalyst ingredient support or the base currently fixed to the front face of photocatalyst ingredient support, and the photocatalyst crystalline which takes the columnar structure of the hollow elongated from this base -- since -- the photocatalyst ingredient which is a becoming photocatalyst ingredient and is characterized by the noble-metals particle being supported by the front face of this photocatalyst ingredient.

[0018] (3) (Two) photocatalyst ingredients characterized by the structure which consists of a photocatalyst particle existing in the interior of said photocatalyst crystalline.

[0019] When acetaldehyde gas is made to decompose using this photocatalyst ingredient that comes to use the photocatalyst of 0.1g of support **** supported on the photocatalyst ingredient support whose catalyst support area it is the photocatalyst

ingredient of either (4), (1) or (3), and is 75mmx75mm The photocatalyst ingredient characterized by the duration for setting acetaldehyde gas concentration in a glass container with a volume of 20l. to 1 ppm or less from 20 ppm being below for 5 minutes to 10 minutes.

[0020] (5) It is the photocatalyst ingredient of either [which said photocatalyst is titanium oxide, and said base is a crystalline nucleus, and is characterized by said noble metals being platinum] (1) thru/or (4).

[0021] (6) photocatalyst ingredient support and the photocatalyst ingredient of either (1) supported on this photocatalyst ingredient support thru/or (5) -- since -- the becoming photocatalyst object.

[0022] (7) The original photocatalyst ingredient production process of obtaining the photocatalyst ingredient with which noble metals are not supported by the front face, It is the photocatalyst ingredient manufacture approach which consists of a noble-metals support process for supporting a noble-metals particle on the front face of the obtained original photocatalyst ingredient. This noble-metals support process The photocatalyst ingredient manufacture approach characterized by including the adsorption process which is immersed in a noble-metals compound solution, adsorbs a noble-metals particle on a photocatalyst ingredient front face, and supports a photocatalyst ingredient, and the desiccation heat treatment process which noble metals dry the photocatalyst ingredient adsorbed and supported, and subsequently heat-treat.

[0023] (8) The (7) photocatalyst ingredient manufacture approaches characterized by establishing the reduction process for returning the noble-metals particle of the oxidation state supported by said photocatalyst ingredient front face after said desiccation heat treatment process.

[0024] (9) (7) or the (8) photocatalyst ingredient manufacture approaches which are characterized by being the compound with which said noble-metals compound contains platinum, such as hexa chloro (platinum VI) acid 6 hydrate.

[0025] (10) It is the photocatalyst ingredient manufacture approach which is the photocatalyst ingredient manufacture approach which serves as the original photocatalyst ingredient production process of obtaining the photocatalyst ingredient with which noble metals are not supported by the front face from a noble-metals support process in order to support noble metals on the front face of the obtained original photocatalyst ingredient, and is characterized by for this noble-metals support process to be a process which makes the front face of a original photocatalyst ingredient support a noble-metals particle with the sputtering method, a vacuum deposition method, or other physical vapor deposition.

[0026] This invention obtains the photocatalyst ingredient of further high activity, when invention-in-this-application persons make the front face of the titanium oxide photocatalyst crystal which has the pillar-shaped hollow structure which already developed and was indicated in the patent application of non-**** mentioned above support a noble-metals particle.

[0027] Said titanium oxide photocatalyst crystal is characterized by putting in a crystalline nucleus into the sol solution of an organometallic compound or inorganic metallic compounds, or solidifying and heat-treating [apply and] a sol solution to a crystalline nucleus, and making it grow up from this crystalline nucleus. Although the titanium oxide crystal itself which has pillar-shaped hollow structure is very already high activity, the activity can be further raised by making this support a noble-metals particle,

and the decomposition effectiveness of organic harmful matter, such as an acetaldehyde, can be raised even twice [about].

[0028] That is, the typical oxide photocatalyst ingredient concerning this invention is a titanium oxide crystal which has the pillar-shaped hollow structure where it was made to grow up from a crystalline germ, and the front face is made to support the particle of noble metals, such as platinum, and the support is immersed in the solution of a noble-metals compound in the photocatalyst ingredient before noble-metals support, makes a noble-metals particle stick to the front face of this photocatalyst ingredient, and is performed by solidifying this by desiccation and heat treatment. Or it carries out by PVD, such as a spatter.

[0029] In this invention, this columnar crystal contains what is straightly extended in the direction of a vertical, the thing extended in the shape of an inclination, the extended thing, the thing which branches in the shape of a branch and is extended, the thing which two or more columnar crystals grew and was united on the way, curving, including all the things that take the spacial configuration of the other shape of a prismatic form, cylindrical, a cylinder, and a column as the configuration of a photocatalyst crystal is pillar-shaped.

[0030] Not only the crystalline nucleus that produced the crystalline nucleus with PVD, such as the sputtering method and a vacuum deposition method, or a CVD method but its class can use a single crystal, the polycrystalline substance, and others widely. Moreover, it is also possible to use as a nuclear alternative the blemish on a thing which is seen by the usual chemical reaction and which is not clearly accepted to be a nucleus like, for example, a substrate, etc. as a crystalline nucleus. Columnar crystal structure grows up one or more columnar crystals on a crystalline nucleus, a crystalline nucleus and the columnar crystal grown up on it grow up to be the same bearing, and the interior of a columnar crystal is characterized by having hollow structure in a typical thing. The photocatalyst which has columnar crystal structure has good contacting efficiency with a decomposition object compared with what has other shape of conventional crystal form, and its resolvability ability improves by leaps and bounds.

[0031] in addition , previously apart from this invention , invention in this application persons removed the outer wall section of a pillar-shaped hollow crystal in part using technique , such as dry etching and wet etching , and proposed the approach of raise resolvability ability as compared with the pillar-shaped hollow crystal which do not remove the outer wall section in the patent application of non-**** with the technique of expose outside the interior used as hollow structure including the structure which consist of a photocatalyst particle (application for patent 2001-392804) . That synergistic effect can raise the resolvability ability of a photocatalyst ingredient further by using together this approach and the manufacture approach of the pillar-shaped hollow crystall luminescence catalyst ingredient noble-metals particle support of this invention.

[0032] In this case, as the technique of exposing the hollow internal structure of said pillar-shaped hollow crystal outside, the dry etching technique, the wet etching technique, and the mechanical approach are effective. There are the physical etching approach and the chemical etching approach in the dry etching technique. As the physical etching approach, there are an ion etching method, the plasma-etching method, etc., and there is the vapor etching method etc. as the chemical etching approach. The etching solution which contains a strong inorganic acid, an oxidant, a fluoride, etc. as a fundamental

presentation is used for the wet etching technique. Furthermore, the mechanical approach is an approach of exposing a hollow internal structure on a front face, by grinding a pillar-shaped hollow crystal. By these approaches, a part of outer wall section of a pillar-shaped hollow crystal is removed, a hollow internal structure is outside exposed, and the photocatalyst function of high activity is obtained.

[0033] Moreover, in the titanium oxide crystal production process of pillar-shaped hollow, by heat-treating with the programming rate of 15 degrees C / min - 105 degrees C / min, or 20 degrees C / min - 100 degrees C / min, the heat-conduction rate which contributes to crystal formation greatly rises, when the crystal consistency of the crystal which constitutes the outer wall section of a columnar structure becomes low, the hollow internal structure of a pillar-shaped hollow crystal is exposed, and high activation of a photocatalyst function is attained.

[0034]

[Embodiment of the Invention] Hereafter, a drawing explains this invention to a detail further. Drawing 1 is the mimetic diagram showing the appearance of the photocatalyst ingredient of this invention. The base 2 to fix this photocatalyst ingredient 10 to the front face of the photocatalyst ingredient support 1 in drawing, It is mainly constituted. the noble-metals particle 5 supported by the front face of this base 2 to the photocatalyst crystalline 3 which takes the columnar structure to elongate, this photocatalyst crystalline 3, and this base 2 -- since -- Are supported on the photocatalyst ingredient support 1, such as various kinds of substrates, such as fiber which has glass, a metal, the ceramics, or network structure. The titanium oxide crystal of a columnar structure grows as a photocatalyst crystalline 3 from the bases 2, such as a crystalline germ, and it has the structure where the noble-metals particles 5, such as platinum, are supported, in the front face of this base 2 and this photocatalyst crystalline 3. In addition, drawing is a mimetic diagram, and especially the magnitude of the noble-metals particle 5 to photocatalyst crystalline 3 grade is emphasized, and also expresses the distribution condition typically.

[0035] Said photocatalyst crystalline 3 can be considered as the configuration in which the structure 6 (henceforth a "crystal grain child") which consists of a photocatalyst particle which shall take a columnar structure (henceforth "pillar-shaped hollow structure") in the air, and is not illustrated inside [photocatalyst crystalline 3] this exists.

[0036] The crystalline nucleus for growing up this photocatalyst crystalline 3 can be used for said base 2 at said photocatalyst crystalline 3, using titanium oxide. Any of a single crystal, the polycrystalline substance, fine particles, the ceramics, the metaled thermal oxidation film, and an oxide film on anode are sufficient not only as the crystalline nucleus which produced the crystalline nucleus with PVD, such as the sputtering method and a vacuum deposition method, or a CVD method but its class. Moreover, it is also possible to use as a nuclear alternative the part which has the condition that are on a substrate and it is different from a substrate like the blemish on a thing which is seen by the usual chemical reaction, and which is not clearly accepted to be a nucleus like, for example, a substrate, and the projection of a foreign matter as a crystalline nucleus. Columnar crystal structure grows up one or more columnar crystals on a crystalline nucleus, a crystalline nucleus and the columnar crystal grown up on it grow up to be the same bearing, and the interior of a columnar crystal is characterized by having hollow structure in a typical thing.

[0037] Although platinum (it is hereafter indicated also as "Pt".) can be used as said

noble metals It is not limited to this, but it changes to Pt, and this invention is palladium (it is hereafter indicated also as "Pd".). Gold (it is hereafter indicated also as "Au".) Silver (it is hereafter indicated also as "Ag".) Iridium (it is hereafter indicated also as "Ir".) Rhodium (it is hereafter indicated also as "Rh".) Ruthenium (it is hereafter indicated also as "Ru".) etc. -- it can also use.

[0038] The photocatalyst ingredient 10 of this invention can constitute the photocatalyst object 20 of the gestalt which is easy to deal with it by being supported on the photocatalyst ingredient support 1, such as various kinds of substrates, such as fiber which has glass, a metal, the ceramics, or network structure.

[0039]

[Function] In drawing 1 , it is fixed to the front face of the photocatalyst ingredient support 1 in the base 2, and the photocatalyst ingredient 10 of this invention is in the condition that the particle of noble metals, such as Pt, was supported, in the front face of the photocatalyst crystalline 3 elongated from this base 2, and this base 2. When the photocatalyst crystalline 3 takes a columnar structure, the surface area is increasing, the photocatalyst function already serves as high activity, but when the noble-metals particle is supported by the front face, the decomposition effectiveness of organic harmful matter, such as an acetaldehyde, becomes still higher, and the decomposition effectiveness of being twice [about] many as this is acquired as compared with the case where a noble-metals particle is not supported.

[0040] For example, it sets into the photocatalyst ingredient 10 of this invention. When acetaldehyde gas is made to decompose using this photocatalyst ingredient 10 that comes to use the photocatalyst of 0.1g of support **** supported on the photocatalyst ingredient support whose catalyst support area is 75mmx75mm The duration for setting acetaldehyde gas concentration in the glass container of volume 20L (liter) to 1 ppm or less from 20 ppm can be shortened even below for 10 minutes and in 6 more minutes. Although the decomposition effectiveness in these conditions showed twice [about] and the considerable improvement in resolvability ability was attained since the concentration of 1 ppm or less was reached in about 15 minutes the place which the conventional powdered photocatalyst takes for about 30 minutes even if it is the case where a noble-metals particle is not supported, the resolvability ability exceeding this further is attained in this invention. On the above-mentioned conditions, as compared with the conventional powdered photocatalyst, the duration of decomposition is shortened by about 1/4 to about 1/5, and one about 4 times thru/or 5 times the decomposition effectiveness of this is obtained in the photocatalyst ingredient of this invention.

[0041] When the excitation electrons excited by the conduction band by the excitation absorption of light to a photocatalyst are collected on a noble-metals particle, it is pooled and an electron hole moves to coincidence toward the organic harmful matter to which it is sticking on the photocatalyst front face, a photocatalyst function becomes high activity by supporting noble metals, such as Pt, to a titanium oxide photocatalyst, because the condition that the recombination probability of an electronic-electron hole pair decreases compulsorily is formed. That is, such recombination is controlled by formation of the charge separation condition of an electronic-electron hole pair, the oxidative degradation of the photocatalysis by surrounding oxygen and a surrounding electron hole and organic harmful matter is promoted, and high sensitivity-ization of photocatalyst activity is attained.

[0042] Drawing 2 is the flow Fig. showing the configuration about one of the photocatalyst ingredient manufacture approaches of this invention. The original photocatalyst ingredient production process P1 for the manufacture approach of this invention to obtain the photocatalyst ingredient in the condition that noble metals are not supported by the front face yet (original photocatalyst ingredient), in drawing, It consists of a noble-metals support process P2 for supporting a noble-metals particle on the front face of the original photocatalyst ingredient obtained according to this process P1. This noble-metals support process P2 the desiccation heat treatment process P22 which dries the photocatalyst ingredient with which this original photocatalyst ingredient was set at the adsorption process P21 which is immersed in a noble-metals compound solution, and adsorbs and supports a noble-metals particle on a photocatalyst ingredient front face, and this process P21, it adsorbed and noble metals were supported, and is subsequently heat-treated -- since -- it is constituted.
[0043] In drawing, the reduction process P23 for returning the noble-metals particle of the oxidation state supported by said photocatalyst ingredient front face can be established after said desiccation heat treatment process P22 by this manufacture approach.
[0044] Suppose that the compound which contains platinum, such as hexa chloro (platinum VI) acid 6 hydrate ("H2PtCl6.6H2O" is indicated hereafter.), as said noble-metals compound is used by this manufacture approach in drawing. As a compound containing platinum, as long as a solution can be prepared, various kinds of things can be used.
[0045]
[Function] In drawing by the photocatalyst ingredient manufacture approach of this invention The photocatalyst ingredient in the condition that noble metals are not supported by the front face yet in the original photocatalyst ingredient production process P1 (original photocatalyst ingredient) is obtained. Subsequently, although a noble-metals particle, such as a compound containing platinum, such as hexa chloro (platinum VI) acid 6 hydrate, is supported by the front face of the original photocatalyst ingredient obtained according to this process P1 in the noble-metals support process P2 Among these noble-metals support processes P2, in an adsorption process P21, it is immersed in a noble-metals compound solution, and a noble-metals particle sticks to this original photocatalyst ingredient on a photocatalyst ingredient front face. The photocatalyst ingredient with which it was supported, and it set subsequently to the desiccation heat treatment process P22, and it adsorbed and noble metals were supported with this process P21 is dried, subsequently it heat-treats, and the photocatalyst ingredient of a columnar structure with which the noble-metals particle of this invention was supported is manufactured.
[0046] Although the photocatalyst ingredient of this invention which the photocatalyst function high-activated rather than the photocatalyst ingredient of the columnar structure which does not support a noble-metals particle by passing through said desiccation heat treatment process P22 can be manufactured, by establishing the reduction process P23 after this process P22 further, and passing through this, it is returned and the noble-metals particle of the oxidation state supported by said photocatalyst ingredient front face can high-activate a photocatalyst function further.
[0047] Drawing 3 is the flow Fig. showing the configuration about other photocatalyst

ingredient manufacture approaches of this invention. The original photocatalyst ingredient production process P1 for the manufacture approach of this invention to obtain the photocatalyst ingredient in the condition that noble metals are not supported by the front face yet (henceforth the "Hara photocatalyst ingredient"), in drawing, It consists of a noble-metals support process P3 for supporting a noble-metals particle on the front face of the original photocatalyst ingredient obtained according to this process P1. This noble-metals support process P3 It is the PVD process P3 which makes the front face of a original photocatalyst ingredient support a noble-metals particle by the sputtering method, the vacuum deposition method, or other PVD. Therefore, the photocatalyst ingredient in the condition that noble metals are not supported by the front face yet in the original photocatalyst ingredient production process P1 (original photocatalyst ingredient) is obtained, a noble-metals particle is supported with this approach by the front face of this original photocatalyst ingredient in the PVD process P3, and the photocatalyst ingredient of this invention is manufactured.

[0048] As noble metals which set at said PVD process P3, and can vapor-deposit into a original photocatalyst ingredient and it can be made to support, various kinds of noble metals, such as Pd, Au, Ag, etc. including Pt, can be used.

[0049] Drawing 4 is the flow Fig. showing the configuration of the original photocatalyst ingredient production process P1 in drawing 2 and drawing 3 . In drawing 4 , the original photocatalyst ingredient production process P1 in drawing 2 and drawing 3 The crystalline nucleus S1 for considering as the base 1 of the photocatalyst ingredient 10 is immersed in the sol solution S2 containing an organometallic compound or inorganic metallic compounds. Or the sol solution S2 which contains an organometallic compound or inorganic metallic compounds in the crystalline nucleus S1 for considering as the base 1 of the photocatalyst ingredient 10 is applied. The gelation process 31 for acquiring the pattern M3 of the photocatalyst ingredient by gelation, The solidification process 32 for drying this pattern M3 acquired according to this gelation process 31, solidifying and acquiring the solidified pattern M4, the heat treatment process 33 for obtaining the original photocatalyst ingredient M5 which has the photocatalyst crystalline 3 which heat-treats the solidified this pattern M4, and takes a columnar structure or pillar-shaped hollow structure -- since -- it is mainly constituted.

[0050] In drawing, the crystalline nucleus S1 for considering as the base 1 of the photocatalyst ingredient 10 according to the gelation process 31 It is immersed in the sol solution S2 containing an organometallic compound or inorganic metallic compounds. The sol solution S2 which contains an organometallic compound or inorganic metallic compounds in the crystalline nucleus S1 for considering as the base 1 of the photocatalyst ingredient 10 is applied, and the pattern M3 of the photocatalyst ingredient by gelation is acquired. Subsequently or according to the solidification process 32 It dries, this pattern M3 acquired according to this gelation process 31 is solidified, the solidified pattern M4 is acquired, subsequently, the pattern M4 this solidified according to the heat treatment process 33 is heat-treated, and the original photocatalyst ingredient M5 which has the photocatalyst crystalline 3 which takes a columnar structure or pillar-shaped hollow structure is obtained.

[0051] Drawing 5 is the flow Fig. having shown the process about the example which supports Pt by two kinds of photocatalyst ingredient manufacture approaches concerning this invention mentioned above. By the approach using the noble-metals compound

solution shown as a wet method in drawing, it is immersed in a hexa chloro (platinum VI) acid 6 hydrate solution, and, subsequently dries for 60 minutes at 150 degrees C, subsequently to the inside of atmospheric air, a pillar-shaped titanium oxide photocatalyst is heat-treated for 120 minutes at 450 degrees C, subsequently hydrogen reduction processing is alternatively carried out for 120 minutes in 450-degree-C ambient atmosphere, and Pt support pillar-shaped titanium oxide photocatalyst is produced. This shows twice [about] as many resolvability ability as this compared with the pillar-shaped titanium oxide photocatalyst which is a start raw material.

[0052] In drawing, on the other hand, Pt particle is supported with physical vapor deposition (PVD) by the spatter, and, as for a pillar-shaped titanium oxide photocatalyst, Pt support pillar-shaped titanium oxide photocatalyst is produced with it. This shows twice [about] as many resolvability ability as this compared with the pillar-shaped titanium oxide photocatalyst which is a start raw material.

[0053] How to produce the columnar structure photocatalyst ingredient which made Pt support with the wet method of drawing 5 is further explained to a detail.

<production of the Hara photocatalyst ingredient> -- the columnar structure photocatalyst ingredient with which the noble metals used as a start raw material are not probably supported with this invention yet is producible using an organometallic compound or inorganic metallic compounds. When producing using an organometallic compound, the titanium oxide crystal which has a columnar structure or pillar-shaped hollow structure is formed in photocatalyst ingredient support front faces, such as various kinds of substrates, such as fiber which has glass, a metal, the ceramics, or network structure, on a crystalline nucleus by putting in a crystalline nucleus into the sol solution which consists of an organometallic compound, or applying a sol solution to a crystalline nucleus, and performing solidification and heat treatment.

[0054] That is, in the solution which mixed and prepared an organic solvent, water, and an acid, stirring organometallic compounds, such as titanium tetra-isopropoxide (henceforth "TTIP"), it drops and mixes and the sol solution which consists of an organometallic compound is obtained.

[0055] Thus, a titanium oxide crystal is formed on a crystalline nucleus by applying the sol solution which is the above, and made and obtained the crystalline nucleus produced by the various producing methods to the crystalline nucleus which was immersed or was produced by the various producing methods into the obtained sol solution, and performing desiccation solidification and heat treatment. As an example, solidification is the attainment temperature of 150 degrees C - 200 degrees C, and the conditions of holding-time 2 hours, and in an electric furnace, heat treatments are the programming rate of 10 degrees C / min, the attainment temperature of 500 degrees C - 600 degrees C, and the conditions of holding-time 2 hours, and can be performed, respectively.

[0056] Among production of a crystalline germ in which the various producing methods are possible, if the approach shown in the patent application (application-for-patent 2001-181969 grade) of non-**** by invention-in-this-application persons is followed, production of the titanium oxide crystal film by evaporative decomposition (henceforth the "SPD method") will add an organic solvent to organometallic compounds, such as TTIP, will consider as raw material liquid, and will be performed by spraying this on photocatalyst ingredient support, such as a substrate, using spraying pyrolysis (SPD) equipment. If the concrete example of production is given, for example as raw material

liquid, an acetylacetone (it is hereafter described as "Hacac".) will be added by the mol ratio (Hacac/TTIP) 1.0 to TTIP, and it will prepare by diluting this with isopropyl alcohol and stirring it. The membrane formation conditions by SPD equipment by considering as atomizing-pressure 0.3MPa, amount of spraying 1.0 ml/sec, the spraying time amount of 0.5ml/time, the substrate temperature of 450 degrees C, and 200 counts of spraying Scanning electron microscope (it is hereafter described as "SEM".) The titanium oxide crystal film which consists of crystals with a magnitude of 30nm - 100nm can be obtained on the surface observation to depend as the crystalline nucleus, i.e., the base, for constituting the start raw material of the photocatalyst ingredient of this invention.

[0057] When using hexa chloro (platinum VI) acid 6 hydrate as a <raw material solution of noble metals to support> Pt compound, this is diluted with water and Pt solution of concentration suitable for adsorption is prepared. Concentration can be adjusted and used for example, for 2x10-3 mol/L (liter).

[0058] Raw material solution concentration can be used from the thing more than 2x10-5 mol/L (liter) extent. The particle diameter of the metal supported by the front face of a original photocatalyst ingredient can be atomized, and the effectiveness of the improvement in photocatalyst functional is acquired, so that solution concentration is low and a raw material solution is thin. Therefore, it is thought possible by changing solution concentration to control the particle diameter of noble-metals particles, such as Pt of a photocatalyst ingredient, in the range of 1 - about 10nm of numbers.

[0059] A original photocatalyst ingredient (titanium oxide photocatalyst ingredient of a columnar structure or pillar-shaped hollow structure) is immersed in the photocatalyst object supported on support, and Pt in a solution is made to adsorb into a <adsorption process-platinum adsorption process> Pt solution until it reaches at equilibrium concentration at a titanium oxide front face (equilibrium adsorption method). In addition, Pt of superfluous concentration is not adsorbed.

[0060] In order to make Pt adsorb and support on a original photocatalyst ingredient, it is also possible to carry out by the proper adsorption technique other than said equilibrium adsorption method, such as an ion-exchange method.

[0061] After supporting Pt into a <desiccation heat treatment process> Hara photocatalyst ingredient, a photocatalyst object is washed with water and Pt solution of the surplus of a original photocatalyst ingredient front face is removed. The glory catalyst object is dried on proper conditions, such as 1 etc. hour, by 150 degrees C. Subsequently, a photocatalyst object is heat-treated according to proper conditions, such as 2 etc. hours, at 450 degrees C in air. In addition, a backwashing-by-water process can be skipped.

[0062] Pt is supported to a <reduction process> titanium oxide photocatalyst, and Pt front face is in an oxidation state in the condition of having heat-treated in air. This is returned in a hydrogen ambient atmosphere. For example, quartz-glass tubing can be filled up with a photocatalyst object, and proper conditions can perform reduction processing for 2 hours using hydrogen-argon mixed gas or pure hydrogen gas etc. at 450 degrees C. The columnar structure photocatalyst ingredient by the wet method which made Pt support is producible through the above processing.

[0063]

[Example] Hereafter, although the test result by the example and the example of a comparison is explained, this invention is not limited to the following examples.

[0064] <Production of crystalline-nucleus and columnar structure photocatalyst

ingredient> neutral detergent, isopropyl alcohol, It sets on the substrate front face with pure water, using as a substrate the alkali free glass which performed washing processing, and a silica fiber filter (ADVANTEC make QR-100). By putting in a crystalline nucleus into the sol solution which consists of an organometallic compound, or applying a sol solution to a crystalline nucleus, and performing solidification and heat treatment, the titanium oxide crystal which has pillar-shaped hollow structure was formed on the crystalline nucleus, and it considered as the titanium oxide substrate and the titanium oxide filter, respectively. Catalyst support area was set to 75mmx75mm, and the amount of titanium oxide support was set to about 0.1g. In addition, it considered as the same catalyst support area and the amount of titanium oxide support below.

[0065] As the adjustment approach of the sol solution which consists of an organometallic compound, 1,3-butanediol:35g, H2O:0.4g, and nitric-acid:0.5g were mixed, and it considered as the solution, and it was dropped, stirring titanium tetra-isopropoxide (it being hereafter described as "TTIP".) 5g in this solution, and stirred in ordinary temperature after that for 4 hours, and the sol solution was obtained.

[0066] Thus, the titanium oxide crystal was formed on the crystalline nucleus by applying the sol solution which is the above, and made and obtained the crystalline nucleus produced by the various producing methods to the crystalline nucleus which was immersed or was produced by the various producing methods into the obtained sol solution, and performing desiccation solidification and heat treatment. Solidification was performed in the dryer on the attainment temperature of 150 degrees C - 200 degrees C, and the conditions of holding-time 2 hours. Heat treatment was performed in the electric furnace on the programming rate of 10 degrees C / min, the attainment temperature of 500 degrees C - 600 degrees C, and the conditions of holding-time 2 hours.

[0067] The production approach of the titanium oxide crystal film by the SPD method was prepared as follows among production of the crystalline germ by the various producing methods according to the approach shown in the patent application (application-for-patent 2001-181969 grade) of non-**** by invention-in-this-application persons. Namely, raw material liquid added the acetylacetone (it is hereafter described as "Hacac".) by the mol ratio (Hacac/TTIP) 1.0 to TTIP, and prepared it by diluting this with isopropyl alcohol and stirring it. atomizing-pressure 0.3MPa, amount of spraying 1.0 ml/sec, the spraying time amount of 0.5ml/time, the substrate temperature of 450 degrees C, and 200 counts of spraying, the membrane formation conditions by spraying pyrolysis (SPD) equipment (YKII Made from a Makeup) came out, and were performed. It was checked that the titanium oxide crystal film produced by the SPD method is constituted from a crystal with a magnitude of 30nm - 100nm by the surface observation by the scanning electron microscope (it is hereafter described as "SEM".).

[0068] Raw material solution hexa chloro (platinum VI) acid 6 hydrate (H2PtCl6.6H2O, best made from the Kanto chemistry) of the noble metals of which <support of noble metals by wet method> 1. support is done was diluted with distilled water, and concentration was adjusted to 2x10-3 mol/L (liter).

[0069] 2. In the adsorption process-platinum adsorption process Pt solution, it was immersed and the above-mentioned titanium oxide substrate with which it comes to support a original titanium oxide photocatalyst ingredient, and the titanium oxide filter were left for 24 hours. Pt in a solution was made to adsorb by this actuation until it arrived at a titanium oxide front face at equilibrium concentration.

[0070] 3. After supporting Pt in a desiccation heat treatment process titanium oxide substrate and a titanium oxide filter, pure water washed these and Pt solution of the surplus of a original photocatalyst ingredient front face was removed. Then, it was made to dry at 150 degrees C for 1 hour, and, subsequently heat-treated at 450 degrees C in air for 2 hours.
[0071] 4. Pt was supported to the reduction process titanium oxide photocatalyst, and in the condition of having heat-treated in air, since Pt front face was in an oxidation state, it returned this in the hydrogen ambient atmosphere. Quartz-glass tubing was filled up with the titanium oxide substrate and the titanium oxide filter, and reduction processing was carried out by 10 capacity % hydrogen-argon mixed gas at 450 degrees C for 2 hours.
[0072] < example 1 With the Pt support photocatalyst ingredient > above-mentioned wet method by the wet method, the pillar-shaped hollow titanium oxide photocatalyst ingredient was made to support Pt, and the titanium oxide substrate and titanium oxide filter ("henceforth a titanium oxide substrate etc.") of this example were produced. However, processing of a reduction process was not performed. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.
[0073] < example 2 With the Pt support photocatalyst ingredient > above-mentioned wet method by the wet method including a reduction process, the pillar-shaped hollow titanium oxide photocatalyst ingredient was made to support Pt, and the titanium oxide substrate of this example etc. was produced. The reduction process was processed in this example. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.
[0074] < example 3 By the Pt support photocatalyst ingredient > PVD by PVD, the pillar-shaped hollow titanium oxide photocatalyst ingredient was made to support Pt, and the titanium oxide substrate and titanium oxide filter of this example were produced. The spatter using RF magnetron sputtering system (Japanese Vacuum technology, SH-350 EL-T06) performed. The membrane formation interior of a room was made to counter Pt target, and said titanium oxide substrate with which it comes to support the titanium oxide photocatalyst ingredient of pillar-shaped hollow structure was laid in it. Pt target of 99.99% or more of target purity was used for the target. After exhausting the membrane formation interior of a room to 10Pa with an oil sealed rotary pump, it exhausted with the turbo molecular pump and the membrane formation interior of a room was made into the predetermined degree of vacuum. Subsequently, argon gas of 99.999% or more of purity was introduced, and the membrane formation interior of a room was made into the argon ambient atmosphere. At this time, whenever [closing motion / of an introductory quantity of gas flow and a main valve] was adjusted so that it might become predetermined argon gas pressure (spatter pressure). And the front face was made to support Pt particle, impressing power to Pt target by DC power supply, performing sputtering of Pt, and rotating the laid titanium oxide substrate by rotational-speed 3rpm. Since not formation of Pt film but support of Pt particle was the purpose, it processed in a short time for 3 minutes. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.
[0075] Example 1 of < comparison Pillar-shaped hollow structure photocatalyst

ingredient > which does not carry out Pt support The titanium oxide substrate of the pillar-shaped hollow structure where above-mentioned Pt particle support processing is not performed etc. was made into the example 1 of a comparison.
[0076] Example 2 of < comparison The powdered photocatalyst ingredient (product made from Japanese Aerosil P-25) of commercial powdered photocatalyst ingredient > marketing was made into the example 2 of a comparison. This was constituted from the titanium oxide particle with a particle size of about 20-30nm by the surface observation using SEM.
[0077] The producing method outline of each example and the example of a comparison is shown in Table 1.
[0078]
[Table 1]

	酸化チタン光触媒の種類	貴金属担持処理の有無および担持方法
実施例1	柱状中空酸化チタン光触媒	湿式法にてPt担持 $H_2PtCl_6 \cdot 6H_2O$溶液に浸漬 →乾燥(150℃、60min) →熱処理(450℃、120min　大気中)
実施例2	柱状中空酸化チタン光触媒	湿式法にてPt担持 $H_2PtCl_6 \cdot 6H_2O$溶液に浸漬 →乾燥(150℃、60min) →熱処理(450℃、120min　大気中) →還元処理(450℃、120minH_2-Ar雰囲気中)
実施例3	柱状中空酸化チタン光触媒	物理的蒸着法にてPt担持 スパッタリング法にてPt担持
比較例1	柱状中空酸化チタン光触媒	Pt担持なし
比較例2	粉末状光触媒	Pt担持なし

[0079] As evaluation of the <characterization approach> photocatalyst function, the decomposition trial of the acetaldehyde which is harmful matter was carried out. After the test method first put the produced titanium oxide photocatalyst object (catalyst support area 75mmx75mm, 0.1g of titanium oxide support ****) into the glass container of volume 20L (liter) and permuted the inside of a container by the controlled atmosphere, it poured in acetaldehyde gas into the container so that it might be set to 20 ppm. Next, germicidal lamp glass with a wavelength of 254nm was irradiated at the titanium oxide photocatalyst object, and the time amount taken to set the acetaldehyde concentration in a container to 1 ppm or less was measured with the gas monitor. SEM performed surface observation of the produced titanium oxide photocatalyst object. 0.03% (CO, CO2, CH4) of carbon dioxide gas and the remainder of the gas presentation of the used controlled atmosphere (Nippon Sanso Corp. make) are moisture 78% [of nitrogen], 21% [of oxygen], and argon 0.9%.
[0080] The characterization result in each example and the example of a comparison is shown in Table 2.
[0081]

[Table 2]

	アセトアルデヒド分解時間(20ppm→1ppm以下になるまでの時間)
実施例1	8min
実施例2	6min
実施例3	6min
比較例1	15min
比較例2	28min

[0082] The result of Table 2 shows the following things. It was checked by SEM observation that the example 1 of a comparison which is the titanium oxide crystall luminescence catalyst ingredient of pillar-shaped hollow structure, and has not performed Pt particle support processing forms the aggregate which consists of a photocatalyst crystalline which is a pillar-shaped hollow crystal with a height [of 3000-5000nm] and a width of 300-500nm. Even if the resolving time of an acetaldehyde was 15min and it was the thing of the phase which a decomposition duration is shortened by about 1/2 as compared with the example 2 of a comparison mentioned later, and whose decomposition effectiveness improves even twice [about], and does not apply the noble-metals particle support technique of this invention, resolvability ability was fully higher than the conventional technique, and it was already shown that it is what has the photocatalyst function of high activity.
[0083] As for the example 2 of a comparison which is a powder-like photocatalyst ingredient, it was checked by SEM observation that many titanium oxide particles with a particle size of 20-30nm exist. The resolving time of an acetaldehyde was 28min.
[0084] Examples 1-3 are titanium oxide crystall luminescence catalyst ingredients which have pillar-shaped hollow structure, and make the front face of the titanium oxide crystall luminescence catalyst of pillar-shaped hollow structure support Pt particle with a particle size of 1-50nm by performing above-mentioned noble-metals support processing to the above-mentioned examples 1 and 2 of a comparison. The result of each example is shown below.
[0085] An example 1 is the photocatalyst ingredient which made the titanium oxide photocatalyst of pillar-shaped hollow structure support Pt particle with a wet method. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.
[0086] The time amount which takes acetaldehyde gas with a concentration [in

predetermined volume space] of 20 ppm to decrease to 1 ppm or less, i.e., the resolving time of an acetaldehyde, is 8min, and as compared with 28min of the example 2 of a comparison, the resolving time could be shortened or less to 1/3, and decomposition effectiveness was able to improve to 3 or more times, and was able to improve the property of the conventional technique very greatly. Moreover, even if compared with 15min of the example 1 of a comparison, the resolving time could be shortened to about 1/2, decomposition effectiveness could improve even twice [about], the property of the titanium oxide photocatalyst ingredient of the pillar-shaped hollow structure by the invention-in-this-application persons made previously could also be improved sharply, resolvability ability was very high, and it was shown that it is the photocatalyst ingredient which has the photocatalyst function of high activity.

[0087] An example 2 is the photocatalyst ingredient which made the titanium oxide photocatalyst of pillar-shaped hollow structure support Pt particle with a wet method including reduction processing. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.

[0088] The time amount which takes acetaldehyde gas with a concentration [in predetermined volume space] of 20 ppm to decrease to 1 ppm or less, i.e., the resolving time of an acetaldehyde, is 6min, and as compared with 28min of the example 2 of a comparison, the resolving time could be shortened about [of a quadrant - 5 minutes] to one, and decomposition effectiveness was able to improve to about about 4 to 5 times, and was able to improve the property of the conventional technique very greatly. Moreover, even if compared with 15min of the example 1 of a comparison, the resolving time could be shortened to 2/5, decomposition effectiveness could improve even by 2.5 times, the property of the titanium oxide photocatalyst ingredient of the pillar-shaped hollow structure by the invention-in-this-application persons made previously could also be improved sharply, resolvability ability was very high, and it was shown that it is the photocatalyst ingredient which has the photocatalyst function of high activity.

[0089] Moreover, the property of an example 2 also endures the resolvability ability of an example 1, and it was shown by reduction processing of the noble metals supported with noble-metals particle support processing by the titanium oxide photocatalyst front face that a photocatalyst function becomes the thing of high sensitivity further.

[0090] An example 3 is the photocatalyst ingredient which made the titanium oxide photocatalyst of pillar-shaped hollow structure support Pt particle by the spatter which is one of the PVD. The obtained photocatalyst ingredient is expected that Pt particle with a particle size of about 1-50nm is supported by the titanium oxide crystal front face of pillar-shaped hollow structure.

[0091] The time amount which takes acetaldehyde gas with a concentration [in predetermined volume space] of 20 ppm to decrease to 1 ppm or less, i.e., the resolving time of an acetaldehyde, is 6min, and as compared with 28min of the example 2 of a comparison, the resolving time could be shortened about [of a quadrant - 5 minutes] to one, and decomposition effectiveness was able to improve to about about 4 to 5 times, and was able to improve the property of the conventional technique very greatly. Moreover, even if compared with 15min of the example 1 of a comparison, the resolving time could be shortened to 2/5, decomposition effectiveness could improve even by 2.5 times, the property of the titanium oxide photocatalyst ingredient of the pillar-shaped

hollow structure by the invention-in-this-application persons made previously could also be improved sharply, resolvability ability was very high, and it was shown that it is the photocatalyst ingredient which has the photocatalyst function of high activity.

[0092] Although Pt was used as support noble metals in the examples 1-3, in addition even if it makes Pd, Au, Ir, Rh, and Ru support on the surface of a photocatalyst, high activation of a photocatalyst function can be attained. This is check ending by experiment.

[0093] In addition, characterization performed other organic compounds not only for an acetaldehyde but for toluene, a xylene, styrene, a trimethylamine, etc., and it was checked that the photocatalyst ingredient of noble-metals support of this invention has the same resolvability ability as the case of an acetaldehyde and the photocatalyst function of high activity also in these.

[0094]

[Effect of the Invention] According to the photocatalyst ingredient concerning this invention, since it is constituted as mentioned above, the photocatalyst function of very high activity can be attained. Moreover, there are no scattering and omission of a photocatalyst ingredient, and handling is easy, it is easy to include in an environmental purge etc., and a manufacturing cost can be reduced.

[0095] By the photocatalyst function of very high activity, the photocatalyst ingredient furthermore applied to this invention has remarkable effectiveness in a clarification function, an antibacterial function, a deordorization function, an antifouling function, etc., and can apply it to environmental purges, such as various air-conditioning equipment or the Shimizu machines, such as an air cleaner, a deordorization machine, and an air conditioning machine, and a water quality purification device, widely.